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**Redox reactions and water quality in cultivated
boreal acid sulphate soils in relation to water
management**

DOCTORAL THESIS IN ENVIRONMENTAL SOIL SCIENCE

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ACADEMIC DISSERTATION

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Abstract

The quality of pore and drainage water influenced by different water management practices was monitored for 2.5 years. The practical aim was to examine how water management affects soil redox processes, and further the off-site hazards caused by cultivated boreal acid sulphate (AS) soils. Soil processes were monitored at three scales: in five soil horizons (the horizon scale), separately in ten monolithic lysimeters (the pedon scale) and in a contemporary field experiment (the field scale). The responses of soil redox status and the quality of pore and discharge water were investigated in waterlogged and effectively drained lysimeters cropped with reed canary grass (*Phalaris arundinacea*). In addition, the impact of waterlogging on soil redox processes was studied in bare lysimeters without plants. The redox potential was continuously monitored and contemporary changes in the chemical quality of pore and discharge water were separately and systematically recorded. This methodology has not previously been used in studies on boreal AS soils. Physical properties of the soil were determined to unravel the ripening processes under different water management systems.

The working hypothesis was that waterlogging results in reduction-induced precipitation of Fe sulphides and a pH rise, and the consequent immobilisation of Al. It thus mitigates the off-site hazards of cultivated boreal AS soils. The results only partly supported this hypothesis. Upon waterlogging, the reduction-induced elevation of pH immobilized Al but concomitantly increased the Fe^{2+} concentration in pore and discharge water. This reaction pattern maintained the acidity of discharge water. This outcome contrasts with the results obtained in warmer environments of the subtropics and tropics. The main reasons for the discrepancy were: 1) the acidic conditions favouring Fe reducers before SO_4^{2-} reducers, 2) the abundance of poorly ordered Fe oxides in boreal actual acid sulphate soil (AASS) horizons, 3) the low temperature, 4) the use of freshwater instead of marine water in waterlogging and 5) low labile organic matter in horizons poor in root material. However, intensified drainage caused the oxidation of potential acid sulphate soil (PASS) layers containing hypersulphidic material. The oxidation proceeded rapidly, although the most reactive monosulphides constituted only 1% of the total sulphides. Ripening processes enhanced the oxidation of sulphides by promoting the diffusion of atmospheric oxygen and convection of NO_3^- into the PASS horizon. In addition, abundant N pools in the PASS horizon may contribute to the oxidation of sulphides by offering raw material for NO_3^- formation. These results suggest that increased N_2O emissions particularly observed in AS soils at least partly result in the oxidation of sulphides by NO_3^- . These results highlight the importance of preventing soil ripening to keep hypersulphidic horizons waterlogged and impermeable.

On the basis of these results, it seems unreasonable to waterlog cultivated boreal AS fields close to the plough layer as a measure to mitigate environmental hazards. There is a risk that Fe^{2+} will leach to watercourses, where it will cause acidity as well as oxygen depletion as a result of oxidation and hydrolysis. The study revealed that acidity retained in the form of secondary minerals retards neutralization and thus counteracts the

mitigation measures. Waterlogging of only the transition and PASS horizons appears to be the most efficient water management option to improve discharge water quality. This practice can especially be recommended on the coast of the Gulf of Bothnia, where reactive monosulphides are abundant and NO_3^- transported into the reduced horizon may concomitantly oxidize Fe sulphides and cause an N_2O emission risk.

Foreword

Acid sulphate soils are a most interesting but also a challenging topic due to their complexity, including soil chemical, physical and biological processes. My journey to becoming a soil scientist studying AS soils from being a water resources engineer began following the advice of my professor, Pertti Vakkilainen, now Professor Emeritus at Aalto University School of Science and Technology. He advised me to take additional studies in soil sciences at the University of Helsinki. The lectures given by Professor Helinä Hartikainen were so interesting that I became fascinated by soil science. My interest in acid sulphate soils with their environmental hazard arose when large fish kills occurred in the rivers running to the Gulf of Bothnia in 2006. On the initiative of Professor Hartikainen AS soils were included in two consortium research projects led by Professor Markku Ollikainen at the University of Helsinki. I was lucky to start as a PhD student in the projects and to combine my water resources engineering background with the study of AS soils in 2007.

This thesis does not make an exception regarding the fact that the most valuable outside contribution to a thesis is provided by experienced scientists in their role of guiding the PhD student. I am grateful that I was subordinated to Professor Hartikainen, Professor Markku Yli-Halla and Dr Asko Simojoki, who all acted as my supervisors. Professor Hartikainen was the leader of the Natural Resources and Environment Postgraduate School, to which I was chosen as a PhD student for four years. I feel that I was always welcome to turn to her with my various enquiries related to profound soil science issues, and I am very grateful to her for her devoted guidance of my PhD studies and most valuable comments on my thesis. I also want to express my warmest thanks to Professor Yli-Halla for introducing me to the world of pedogenesis and acid sulphate soils. His guidance throughout my PhD study was of utmost importance, both in theoretical and practical issues, as well as also his keeping an eye on the lysimeters daily on his way to his office. For example, he alerted me to the threat of breakage of the glass roof due to a heavy snow load following a winter snow storm in 2009. I am also most grateful to Dr Simojoki for his assistance with the study plan, his advice with probes and data loggers, and for familiarising me with the data-processing program SURVO to replace Microsoft Excel when the working capacity of the latter exhausted. In addition, I highly appreciate the opportunity for lengthy discussions of theoretical soil physical issues, as well as his help in solving many practical problems and also being a very precise co-writer. I also want to express my gratitude to Dr Simojoki for his valuable advice for improving the figures in my thesis.

Special thanks to Professor Miloslav Šimek and Václav Křišťůfek at Ceske Budejovice for microbial analysis of AS soils, Ossi Knuutila for preparing Pt electrodes and for creating a measurement program for the data loggers, and Janne Toivonen for conducting sulphur species analyses at Åbo Akademi University. I am also grateful to Dr Hannu Rita for his inspiring lectures, which gave me an idea to use the approach of

similarity in my thesis, and especially his guidance in applying the similarity approach in the correct way. All of them were co-writers in the respective papers.

Professor Martin Rabenhorst and Professor Leigh Sullivan, the reviewers of my thesis, are gratefully acknowledged for their most valuable comments and constructive criticism.

The experimental part of my study, comprising the establishment of the lysimeter experiment and field monitoring, lysimeter maintenance, the development of the measurement methods, analyses, and the handling procedures for the substantial amount of data, was very laborious. The amount of work was so huge that I wouldn't have managed without the help of many others. Regarding the establishment of the experiment, I would like to express my gratitude to Matti Ylösmäki from MTT for producing the cutting bit, which was tailor made for digging the soil monoliths for the lysimeters, and Heikki Oikairinen for digging them from the Patoniitty field in Viikki. In addition, many thanks to Arto Nieminen for his help in many technical issues, such as the drilling of the ceramic tips for the salt-bridges, and to Daniel Richterich for taking care of the space where the lysimeters were located, *e.g.* protecting the lysimeters from damage caused by rats, a threat which I could not imagine to be of any risk.

The ten lysimeters would not have overcome the two and half years' experimental period without tender care. This meant daily irrigation and water maintenance during the summers, and during the winters measures had to be taken to protect the subsoils of the lysimeters from freezing. Olga Nikolenko deserves my special thanks for assisting in the maintenance of the lysimeters and in sampling, as well as in the physical and chemical analyses, such as the measuring of elements by ICP-OES. My warmest thanks also go to Kenedy Epie Etone for helping in the establishment and maintenance of the lysimeter experiment. I additionally want to thank the trainees from HelTech and the students Anja Lammi, Johanna Muurinen and Miira Jääskeläinen for assisting in the maintenance of the lysimeter experiment, water sampling and analyses. In the various chemical analyses, I greatly appreciate the help and assistance of Miia Collander, Marjut Wallner, Maija Ylinen and Päivi Ekholm. Many thanks to Miia for her expertise in photographing the lysimeters and their dismantling. I have had an opportunity to get to know wonderful persons studying soil science, including Petra Tallberg, Salla Venäläinen, Mari Rätty, Paula Luodeslampi, Maria Lehtimäki and Virpi Siipola, while we have shared an office in the cellar of D-building at the Viikki campus. Thank you for your company. In addition, as a doctoral student, I was allowed to take part in national and international seminars and congresses, where I made many long-lasting friends, and I wish to thank all of them for their contributions relating to our discussions.

Many thanks to Dr Roy Siddall for the language revision of my published papers and the thesis.

Just after having completed the experimental part of my thesis study, I started work as an executive director of the Finnish Drainage Foundation. At that stage, only one of the four papers was published. I am greatly thankful to Timo Kauppi, the Chairman of the Board of the Finnish Drainage Foundation, and all the members of the Board for giving

me the opportunity to write the remaining papers alongside my daily tasks at the foundation.

I am deeply grateful for the financial support of this study provided by the “Bioenergy, electricity and emission trading markets” (BEET) project funded by the Academy of Finland, the “Bioenergy cropping chains - the production of raw materials in an environmentally and economically sustainable way” project of the Faculty of Agriculture and Forestry of the University of Helsinki, the Natural Resources and Environment Postgraduate School, the “CATERMASS Life+” project, the Oiva Kuusisto Foundation and the Finnish Drainage Foundation. The travel grants awarded by the University Helsinki and Maa- ja vesiteknikan tukiry gave me an opportunity to take part in the scientific conferences. Many thanks for that.

The process of writing a thesis has not only meant hard work but has also meant moments of great delight when succeeding in and accomplishing minor tasks and reaching milestones of the project, and especially so when achieving scientific insights and finding pieces of new knowledge. For this, I am grateful to all of the above-mentioned persons and all other persons not mentioned but who have contributed in the completion of the thesis.

Even though I have been very devoted to and strictly tied to my PhD studies, my heart has been always with my parents and family. The steadfast support and love of Veijo and my children Lauri, Antti, Sanni and Olli has given me the strength during these years and enabled me to reach the target.

Helsinki, September 2015

Seija Virtanen

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List of original publications and participation

This thesis is a summary and discussion of the following articles, which are referred to by their Roman numerals:

- I Šimek M., Virtanen S., Křišťůfek V., Simojoki A. & Yli-Halla M. 2011. Evidence of rich microbial communities in the subsoil of a boreal acid sulphate soil conducive to greenhouse gas emissions. *Agriculture, Ecosystems & Environment* 140:113-122.
- II Virtanen S., Simojoki A., Knuutila O. & Yli-Halla M. 2013. Monolithic lysimeters as tools to investigate processes in acid sulphate soil. *Agricultural Water Management* 127:48-58.
- III Virtanen S., Simojoki A., Hartikainen H. & Yli-Halla M. 2014. Response of pore water Al, Fe and S concentrations to waterlogging in a boreal acid sulphate soil. *Science of the Total Environment* 485-486:130-142.
- IV Virtanen S., Simojoki A., Rita H., Toivonen J., Hartikainen H. & Yli-Halla M. A multi-scale comparison of dissolved Al, Fe and S in a boreal acid sulphate soil. *Science of the Total Environment* 499:336-348.

In addition, some unpublished data are presented.

The author's contribution:

Paper I

The basic idea to compare the microbial communities in an AS soil profile with those in a non-AS soil profile came from Markku Yli-Halla. The study was jointly designed by Seija Virtanen, Markku Yli-Halla, Asko Simojoki and Miloslav Šimek. Seija Virtanen designed and was responsible for soil sampling and analysis of the chemical and physical properties of the soils. Microbial analyses were jointly designed with Professor Šimek, and he carried them out together with Václav Křišťůfek. Seija Virtanen was the corresponding author, interpreted the results together with the co-authors and contributed to the writing of the article.

Paper II

Seija Virtanen, Asko Simojoki and Markku Yli-Halla designed the sampling of monoliths. The lysimeters and the piston were designed and constructed by Seija Virtanen. Together with Asko Simojoki, she designed the monitoring protocol for the probes, and Ossi Knuutila carried out the programming for the Agilent data loggers and made Pt electrodes used in the study. Seija Virtanen was responsible for all the experimental work during the experiment. She conducted the data analyses, interpreted the results together with the co-authors and wrote the paper. The co-authors critically commented on all versions of the paper.

Paper III

Seija Virtanen designed the study and was responsible for all the experimental work, conducted the data analyses and wrote the paper. She interpreted the results together with the co-authors and they critically commented on all versions of the paper.

Paper IV

The original idea for the paper was developed by Seija Virtanen. The idea to use the similarity approach came from lectures given by Hannu Rita. Seija Virtanen designed the study and was responsible for all the experimental work, except the sulphide analysis, which was carried out by Janne Toivonen. The interpretation of similarity results was performed by Seija Virtanen and Hannu Rita. Other results were interpreted together with Helinä Hartikainen, Markku Yli-Halla and Asko Simojoki. Seija Virtanen conducted the data analyses and wrote the paper. The co-authors critically commented on all versions of the paper.

Symbols and abbreviations

The key concepts of this thesis related to cultivated boreal AS soils

AS soil = Acid sulphate soil is characterised by an extremely acidic soil horizon(s) or/and a horizon(s) containing sulphidic material in such amounts that they have been or can be transformed to extremely acidic soils in oxidizing conditions. An AS soil pedon may comprise both extremely acidic (AASS) and non-acidic/neutral (PASS) horizons.

AASS = Actual acid sulphate soil contains extremely acidic soil horizons due to the oxidation of sulphidic material therein.

PASS = Potential acid sulphate soil refers to a non-acidic/neutral soil or soil horizon(s) that can be transformed into AASS soil due to surplus sulphides in relation to neutralizing agents.

Cultivated boreal AS soils = The majority of AS soils in Europe are located on the coast of the Baltic Sea in Finland (Andriessse and van Mensvoort 2006). The area belongs to the boreal biogeographical region of Europe (EEA, 2011) and in the boreal and hemiboreal zones comprising large areas in the Northern Hemisphere (Brandt 2009). In this study, cultivated boreal AS soils refer to the fields on the coast of the Baltic Sea with AS soils.

Abbreviations

AVS = acid volatile sulphur
BS = basal respiration
C = culturable cell population density
C/T = culturable to total cell ratio
CBE = charge balance error
CFU = colony forming unit
COLE = coefficient of linear extensibility
DEA = denitrifying enzyme activity
DHA = dehydrogenase activity
DOC = dissolved organic carbon
DNRA = dissimilatory nitrate reduction to ammonium
GHG = greenhouse gases
EC = electrical conductivity
HWB = bare high water table treatment
HWC = cropped high water table treatment
LWC = cropped low water table treatment
OC = organic carbon
OM = organic matter
PFP = preferential flow paths
PSD = pore size density
RCG = reed canary grass

SHE = standard hydrogen electrode
 SIR = substrate induced respiration
 T = total number of bacteria
 TEA = terminal electron acceptor
 TN = total dissolved nitrogen in pore water
 WRC = water retention curve
 XRD = X-ray diffraction analysis

Symbols

$\hat{\theta}$ = potential similarity
 C_{org} = organic carbon in soil, g kg^{-1}
 E^0 = standard electrode potential, mV
 E_h = soil redox potential relative to SHE at 298 K, mV
 E_{h7} = soil redox potential relative to SHE at 298 K and pH 7, mV
 E_m = soil redox potential, mV
 E_{ref} = redox potential of the reference electrode relative to SHE at 298 K, mV
 EC_{dw} = electrical conductivity of discharge water, dS m^{-1}
 EC_{gw} = electrical conductivity of groundwater, dS m^{-1}
 EC_m = electrical conductivity of soil, dS m^{-1}
 EC_{pw} = electrical conductivity of porewater, dS m^{-1}
 Fe_o = iron extracted by acid ammonium oxalate (pH 3) in the dark, g kg^{-1}
 f_{pH} = correction factor for converting E_h to pH 7
 f_t = temperature correction factor for the reference electrode
 $G(r)$ = cumulative pore size density function
 $g(r_i)$ = pore size density for an equivalent pore radius i
 k = number of subcurve, $i = 1, 2$
 K_s = saturated hydraulic conductivity, m day^{-1}
 Mn_{tot} = total manganese in soil, g kg^{-1}
 N_{min} = inorganic nitrogen in soil, g kg^{-1}
 N_{tot} = total nitrogen in soil, g kg^{-1}
 pH_{fresh} = pH of fresh soil in water, (1:1)
 pH_{inc} = pH of incubated soil in water, (1:1)
 pH_m = soil pH *in situ*
 pH_{dw} = pH of discharge water
 pH_{gw} = pH of groundwater
 pH_{pw} = pH of pore water
 r_i = radius of equivalent pore size in class i , μm , $i = 1, N$
 S_{tot} = total sulphur in soil, g kg^{-1}
 T_a = air temperature, K
 T_{gw} = temperature of groundwater, K
 T_m = soil temperature, K
 w_i = weighing fraction of WRC sub-curves 1 and 2, $\sum w_i = 1$, $i = 1, 2$
 ε = volumetric water content of soil, $\text{m}^3 \text{m}^{-3}$
 ε_i = water content at the equivalent radius i calculated from the WRC, $\text{m}^3 \text{m}^{-3}$
 ε_s = saturated water content, $\text{m}^3 \text{m}^{-3}$
 θ_1, θ_2 and θ_3 = similarity levels
 Ψ_i = matric suction corresponding to the equivalent radius of a pore size class, cm

1. Introduction

1.1. Recognition of boreal acid sulphate (AS) soils and their problematic characteristics

In boreal areas, acid sulphate (AS) soils were recognised not later than in the last century (Frosterus 1913) because of their odd properties such as the smell of rotten eggs and charcoal black colour, which caught people's attention (Pons 1973). Despite these exceptional properties, AS soils were attractive for cultivation, because they were free of stones, in contrast to typical field soils in Finland (Purokoski 1959). In earlier times, when soils were reclaimed for fields, the uppermost peat layers were typically burned to release nutrients (Talve 1979). However, when the peat cover was lost, oxygen penetration into the horizons containing sulphidic materials became easier. Furthermore, as precipitation exceeds evaporation, the fields have to be drained. In boreal conditions, especially in spring and autumn, the surplus of water needs to be rapidly conveyed away from fields. In earlier times, when drainage was only maintained by shallow open ditches, it already promoted the oxidation of sulphidic materials and the formation of sulphuric acid, as indicated by massive fish deaths as early as in 1834 (Manninen 1972). However, owing to the lack of knowledge, these hazards were not linked to AS soils.

After Finland gained independence in 1917, farming started to rapidly develop and the target was to achieve self-sufficiency in foods. To increase the productivity of cultivation, new techniques such as subsurface drainage were promoted, adopting knowledge from countries such as England, Germany and Sweden (Aarrevaara 1993, p. 65, 80, 99). As early as in 1925, the Finnish Drainage Association established experimental fields to establish planning criteria for subsurface drain depths and spaces for non-AS soils and AS soils (Keso 1930, 1940). Before this, the criteria used in the elsewhere in Europe were mainly adopted (Hallakorpi 1917, p. 75-80). Frosterus (1913) recognised the poor growth of plants in certain areas that were later recognised as AS soils. However, he concluded that it was caused by the massive soil structure rather than by soil chemical properties. Later, Aarnio (1928a) noted the relationship between a high sulphur content and sulphuric acid formation and the poor growth of plants, but not the connection between land drainage and environmental hazards. Nevertheless, he supported the establishment of field experiments to develop proper guidelines for drain spacing and depths on AS soils (Aarnio 1928b).

Based on his field experiment, Keso (1940) proposed a shallower subsurface drainage depth for AS soils (1 m) than that generally used for non-AS soils (1.2 m). The main reasoning was that the soil shrinkage brought about large water-conveying cracks, which further led to extraordinarily wide drain-spacing guidelines of up to 100 m for AS soils. The corresponding spacing used in ordinary clay soils was only 10–25 m (Keso 1924). However, Keso's experiment was carried out in southern Finland on a heavy clay AS field, where the capillary rise was quite slow (Keso 1940, 1941), similarly to AS soils in

central Sweden (Wiklander and Hallgren, 1949). Therefore, deep drainage was thought to be unnecessary. Regarding silty AS soils in northern Sweden and Ostrobothnia in Finland, proper drainage appeared to be necessary to stop the capillary rise of water and to prevent the accumulation of Al salts in the soil surface, as well as to promote their leaching to make field productive (*e.g.* Kivinen 1944, Wiklander *et al.* 1950a). The drain depths were generally 1.0 to 1.2 m, but in peat soils as much as 1.5 m (Saavalainen 1986).

In Ostrobothnia, mainly in the 1950s to 1970s, dredging and poldering of low-lying fields were implemented by authorities to minimize flooding hazards and to establish proper main drainage in order to achieve efficient field drainage (*e.g.* Manninen 1972, Österholm *et al.* 2005). In the 1960s, subsurface drainage was mechanized, and in the 1980s, new techniques such as trenchless drainage machines and plastic pipes were introduced in Finland (Aarrevaara 1993, p. 196). Consequently, fields in AS soils were also subsurface drained by farmers more than ever before. As result of all these operations, environmental hazards in water courses became more common, which gave an impetus for studies on drainage-induced changes in the water quality of the recipient waters in AS soil areas, such as acid loading, and their lifespan (*e.g.* Manninen 1972, Österholm 2005), the isotopic ratios of sulphur in leaching water (*e.g.* Åström and Spiro 2000), the quantities of leaching metals (*e.g.* Åström and Björklund 1995, Joukainen and Yli-Halla 2003), and their ion species (*e.g.* Nystrand and Österholm 2013). Furthermore, in fields, the drainage-induced changes in sulphur species were determined (*e.g.* Nordmyr *et al.* 2006, Boman *et al.* 2008, Boman *et al.* 2010).

1.2. Mitigation options to reduce environmental problems caused by AS soils

Although the off-site hazards attributable to AS soils were not recognised in earlier times, the on-site hazards were apparent. Consequently, liming experiments were already established in Finland in 1920 (*e.g.* Brenner 1929). Thereafter, the effect of liming of cultivated AS soils on the growth of crops has been widely studied (*e.g.* Kivinen 1944, Palko 1988). The extensive liming of AS fields is found to neutralize the acidity of run-off water by 5–35% (Palko and Weppling 1994) or less (Åström *et al.* 2007). The effect of lime filter drains is reported to be uncertain or only short term (Rapport *et al.* 2000, Åström *et al.* 2007). On the other hand, the liming of discharge waters requires a huge amount of liming materials and involves high costs. It also results in the precipitation of SO_4^{2-} and Al compounds on the bottom of watercourses, which exerts deleterious effects on aquatic life (*e.g.* Weppling and Iivonen 2005). The impact of AS soils (*e.g.* Palko 1986, Yli-Halla and Palko 1987, Harmanen 2007, Fältmarsch *et al.* 2009) and their liming (Palko *et al.* 1988) on the concentration of various elements in cultivated plants has also been investigated. The studies have confirmed the need for liming to be substantial. Interestingly, the frequency of re-liming is found to be lower in subsurface-drained fields than in those drained by open ditches (Palko 1988, Palko and Weppling 1994). This is

attributable to the fact that the deeper sub-surface drainage lowers the groundwater table more than does the conventional shallow open ditch drainage. By restricting the capillary rise of acid water to the plough layer, it diminishes the need for liming, rendering the subsurface drainage more economical for farmers.

In Finland, massive fish kills in the rivers flowing into the Gulf of Bothnia in 2006 (Österholm 2008) triggered several projects aimed to mitigate the off-site hazards from AS soils (*e.g.* Engblom *et al.* 2014, Österholm *et al.* 2015). The present thesis study exploring soil processes in AS soils and aiming at the mitigation of discharge water quality was also included among these projects. The poor ecological status of rivers and floods running into the Gulf of Bothnia from catchments consisting of large AS soils areas led to the formulation of a mitigation strategy (Nuotio *et al.* 2009). Furthermore, the previous AS soil mappings (*e.g.* Purokoski 1959, Puustinen *et al.* 1994) were complemented and defined with more detailed information, classifying soils according to their environmental risks (Edén *et al.* 2012). Concomitantly with the increasing interest in environmental issues at national and international levels, the focus of studies on the off-site effects also became wider. In addition to the relationship between AS soils and the quality of discharge waters, attention has been paid to the generation of greenhouse gases (GHG) (Denmead *et al.* 2010, Macdonald *et al.* 2011, Simojoki *et al.* 2012) and to human health (Ljung *et al.* 2009, Fältmarsch 2010).

The reclamation and drainage of a virgin PASS area by conventional subsurface drains causes more extensive hazards than shallower open ditch drainage. Thus, to slow down the acidification process and acidity peaks after reclamation, Palko (1994, p. 32) proposed a two-stage practice whereby trenches are dug in the first stage and the subsurface drainage is installed 5–8 years later. However, subsurface drainage is commonly installed in open ditch drained fields where AASS horizons have already developed to various depths. At the beginning of the 1990s, the oxidation of cultivated AS soils had reached an average depth of 1.23 m (Puustinen *et al.* 1994, Yli-Halla *et al.* 2012). This approximately corresponds to the depth of subsurface drains in Finland. Actually, Palko (1994, p. 33) recommended controlled drainage as a mitigation method for cultivated ripe AS soils. This measure, where subsurface drains are assisted by control wells for the storing of water in fields, has already been used to diminish the nutrient loads from agricultural fields in boreal conditions (Paasonen-Kivekäs *et al.* 1998). At the end of the 1990s, its applicability was investigated in two different AS areas. In a field where the PASS horizons were located at a relatively shallow depth, no improvement in water quality could be detected, because the raising of the groundwater to a higher level failed (Åström *et al.* 2007). However, on a field where the PASS horizons were located at a greater depth, controlled drainage to some extent improved the quality of the discharge water (Bärlund *et al.* 2005). Therefore, controlled drainage is widely considered to be superior to conventional subsurface drainage. However, a good ecological status of the rivers has not been attained, and more efficient methods for the mitigation of environmental hazards caused by cultivated AS soils are therefore still urgently needed.

The aquatic life and ecosystems in rivers running through AS areas are susceptible to acidity and suffer from acid loadings. Promising mitigation methods have been developed,

but under conditions differing decisively from those prevailing on the coast of Baltic Sea, for instance in terms of the salinity and alkalinity of the water, temperature and precipitation. For example, in warmer conditions, the waterlogging of AS fields by oceanic water or freshwater has improved water quality mainly due to the neutralization of soil acidity by reduction reactions (*e.g.* Johnston *et al.* 2012, Johnston *et al.* 2014). In boreal conditions, the oxidation of sulphidic materials and acid leaching have been widely studied in fields and also in the laboratory (*e.g.* Hartikainen and Yli-Halla, 1986, Åström and Björklund 1997), but less attention has been paid to the reduction reactions, particularly in cultivated AS soils. Although the oxidation of Fe sulphides causes hazards, reduction reactions do not self-evidently mean the commencement of reverse processes that mitigate the hazards, because irreversible pedogenic transformations may already have occurred in the soil. Therefore, a better understanding of the reduction of ripe AS soils by means of waterlogging in boreal conditions would provide better tools to handle this challenging problem. To avoid environmental hazards related to land use such as farming or building, locally applicable information is urgently required, but has not previously been systematically assessed.

1.3. Formation of Fe sulphide sediments on the coast of the Baltic Sea

The parent sediments of AS soils were formed during the Litorina Sea Stage of the Baltic Sea, when the oceanic water flowed through the Danish straits into the Baltic Basin. This saline period followed the Ancylus Lake stage and started about 7400–7300 BP on the coast of southern Finland and ca. 7000 BP in the Gulf of Bothnia (Eronen 1974). The salinity was at its highest about 7000–6000 BP, when it exceeded 20‰ near the Danish straits and was about 8‰ in the Gulf of Bothnia and in the area of Helsinki in the Gulf of Finland (Hyvärinen *et al.* 1988). However, in the Litorina Sea stage, in the deep water layers below the halocline, the salinity in the Gulf of Bothnia was 13‰ (Georgala 1980). The Litorina Sea stage was followed by the less saline Limnea Sea about 4000 BP (Hyvärinen *et al.* 1988). During this period, sulphidic materials started to become covered by non-sulphidic sedimentary material.

In the Litorina Sea, the salinity and SO_4^{2-} concentration were higher than in the present Baltic Sea. In the anoxic or intermittently oxic sea bottom, the diffusion of SO_4^{2-} into the anoxic sediment resulted in the formation of Fe sulphides (Georgala 1980, Sohlenius and Öborn 2004). Furthermore, the warm climate and the intrusion of saline water induced the upward flow of nutrient-rich water, thereby favouring eutrophication (Sohlenius *et al.* 1996). The high primary production supplied Fe^{3+} - and SO_4^{2-} -reducing microbes with organic matter, which led to the formation of Fe^{2+} and H_2S (Eq. 1 and 2, Table 1). The reaction of H_2S or HS^- with Fe oxides or Fe^{2+} resulted in the formation of aqueous or solid FeS (Eq. 3 and 4, Table 1). Further reaction steps of FeS were dictated by the conditions in the sea bottom. In marine sediments, mackinawite (FeS), generally

Table 1. Selected anaerobic overall redox reactions in the sea bottom conducive to PASS sediment formation.

Reaction step	Reaction	Equation number
Oxidation of organic matter	$4 \text{FeOOH} + \text{CH}_2\text{O} + 8 \text{H}^+ \rightarrow 4 \text{Fe}^{2+} + \text{CO}_2 + 7 \text{H}_2\text{O}$	[1] ^a
	$\text{SO}_4^{2-} + 2\text{CH}_2\text{O} \rightarrow \text{H}_2\text{S} + 2\text{HCO}_3^-$	[2] ^b
Formation of FeS	$\text{Fe}^{2+} + \text{H}_2\text{S} \rightarrow \text{FeS} + 2\text{H}^+$	[3] ^c
	$\text{Fe}^{2+} + 2 \text{HS}^- \rightarrow \text{Fe}(\text{HS})_2 \rightarrow \text{FeS} + \text{H}_2\text{S}$	[4] ^c
Formation of FeS ₂	$\text{FeS} + \text{H}_2\text{S} \rightarrow \text{FeS}_2 + \text{H}_2$	[5] ^d
	$\text{FeS} + \text{S}_n^{2-} \rightarrow \text{FeS}_2 + \text{S}_{n-1}^{2-}$	[6] ^e

^a Stumm and Morgan 1996, ^b Berner 1984, ^c Rickard 1995, ^d Rickard 1997, ^e Luther 1991.

thought to be the first formed, is transformed to greigite (Fe₃S₄) and/or through different pathways to pyrite (FeS₂). However, in salt marshes (Howarth 1979) and in coastal oceanic AS soils (Burton *et al.* 2011), FeS₂ is reported to be formed without any precursor. Various mechanisms for pyrite formation have been presented (comprehensively reviewed by Rickard and Luther 2007). Only the reactions with FeS and H₂S (Eq. 5) and the polysulphide pathway (Eq. 6) have been isotopically validated, but pyrite nucleation following crystal growth from Fe²⁺ and S²⁻ might also occur (Rickard and Luther 2007).

In marine sediments, Fe sulphides mainly occur as FeS₂ (*e.g.* van Breemen 1973, Dent and Pons 1995, Fanning *et al.* 2010). However, the Litorina sediments on the coast of the Gulf of Bothnia can be exceptionally high in FeS, its proportion being up to 80% (Georgala 1980) or even up to 88% (Boman *et al.* 2010). In contrast, in soils formed in the Litorina Sea in southern Sweden, Fe sulphides are reported to occur mainly as FeS₂ (Sohlenius and Öborn 2004). According to Boman (2008), in boreal conditions, FeS₂ was probably formed during the Litorina stage mainly by the polysulphide pathway (Eq. 6, Table 1). Because in this reaction route the oxidation or dissolution of FeS is needed prior to pyrite formation, the exceptionally high FeS concentration in some boreal Litorina sediments can partly be explained by the hindrance of these processes in these areas. In the Litorina Sea stage, in the bottom of the Gulf of Bothnia, rapid sedimentation provided an abundant supply of Fe³⁺ for reduction, but also restricted the diffusion-based SO₄²⁻ supply from brackish seawater into the sediment, causing the lack of elemental S to oxidize FeS to FeS₂ (Georgala 1980, p. 142, Boman 2008, p. 42). In addition, Fe complexed in humic substances that leached to the Litorina Sea might have contributed to the abundance of Fe, causing a high Fe³⁺/ SO₄²⁻ ratio in the sea bottom, and resulting in highly reduced conditions that also contributed to the preservation of FeS in the sediment (Boman *et al.* 2010).

The weight of the glacier pressed the earth's crust hundreds of metres downwards. Upon melting of the ice cover, the crust started to rebound due to adjustment of the isostatic balance. Consequently, the level of the Litorina Sea lowered and new land was uplifted from the sea. However, in southern Finland, the Litorina Sea level rose again

(transgression) between about 7500–6100 BP (Korhola 1995) due to the rise in the oceanic sea level. In the Helsinki region, the rise was about 2–4 m and sediments that had already uplifted were submerged again (Eronen 1974). On the contrary, on the coast of the Gulf of Bothnia, the land uplift rate exceeded the sea level rise and no transgression occurred (Hyvärinen *et al.* 1988). As result of the high uplift rate and the flat topography, the largest areas on the Finnish coast that have emerged from the sea since the Litorina Stage, totalling 50 000 km², are located in this area (Edén *et al.* 2012).

1.4. Classification of acid sulphate (AS) soils

Cultivated boreal AS soils commonly consist of an extremely acidic horizon(s) (AASS horizon(s)), below which are permanently water-saturated circumneutral horizons containing sulphidic material. In virgin AS soil areas, sulphidic horizons may also reach up to the topsoil. During the formation of sulphidic sediments, the alkalinity produced in reduction reactions, generally in the form of bicarbonate (HCO₃⁻) (Eq. 2, Table 1), may become lost in the sediments, for instance by diffusion to the water column. If this occurs, the sediments may form potential acid sulphate soil (PASS). PASS contains enough sulphides to lower the soil pH below 4, and it is termed hypersulphidic (IUSS 2014). The acidity is caused by the oxidation of sulphides (see chapter 4.4.2) to sulphuric acid and by the hydrolysis reactions of Fe^{2+/3+}.

AS soils are typically classified nationally (*e.g.* Pons 1973, Dekimpe *et al.* 1988, Sullivan 2012) and/or according to international soil classification systems (*e.g.* IUSS 2014, Soil Survey Staff 2014). According to Soil Taxonomy the most prevalent types of AS soils in Finland are *Typic Sulfaquepts* and *Sulfic Cryaquepts* (Yli-Halla *et al.* 1999). In this thesis, the criteria of the World Reference Base for Soil Resources (IUSS 2014) are used in connection with the soil monoliths, but national classification is applied if it is used in the references. Regarding soil temperature regimes, the definitions of Soil Taxonomy (Soil Survey Staff 2014) are used, because they are not included in the WRB.

1.5. Ripening of AS soils

Since the Litorina Sea stage, parts of the sea bottom on the Finnish coast of the Baltic Sea have gradually turned into dry land. At present, the absolute uplift rate is 3–9 mm/year (Johansson *et al.* 2004). The reclamation of these soils for cultivation results in soil ripening, which refers to the physical, chemical and biological changes during the transformation of the water-saturated sediment to dry land soil as defined by the Dutch soil scientists Pons and Zonneveld (1965). When reclaimed, the ripening of a 10-cm PASS horizon to an AASS horizon may take five to ten years (*e.g.* Keso 1940). This is a very short period compared to the timespan of pedogenesis in other types of soils, where the development of horizons may even take several centuries (van Breemen and Buurman

2002). Drainage will initiate the ripening processes in AS soils. However, dewatering of massive PASS by gravity is limited because of the extremely low saturated hydraulic conductivity (K_s) (*e.g.* Joukainen and Yli-Halla 2003, Johnston *et al.* 2009a) and the high water retention capacity, particularly in AS soils rich in clay (Bärlund *et al.* 2004). However, when drainage is assisted by transpiration, water in micropores will also be partly extracted and ripening of the soil will progress faster (Dent 1986).

During the ripening process, shrinkage of massive soil in PASS horizons leads to cracking of the soil and initiates the development of typical well-structured AASS horizons *e.g.* (Frosterus 1913, Andersson 1955, Johnston *et al.* 2009a). In contrast to vertic soils characterized by strong shrink-swell properties, shrinkage in AS soils is mainly irreversible. This is due to the loose card-house structure of the sediments consisting of clay platelets that slowly settled on the sea bottom in conditions characterised by a pH lower than 7 and contributed to by a high electrolyte concentration (Koorevaar *et al.* 1983, p. 22). When the card-house structure collapses as result of drying, this cannot be reversed by re-saturation.

Secondly, the pronounced shrink-swell properties of vertic soils are attributable to expanding clay minerals, most typically to smectite. In boreal AS sediments, swelling clay minerals are only present in small amounts (Georgala 1980, Öborn 1989, Åström and Björklund 1997), evidently due to the slow weathering processes on the sea bottom. However, when PASS horizons turn to AASS horizons, the swelling properties may develop concomitantly with mineral weathering and the formation of jarosite. According to Ivarson *et al.* (1978), the potassium needed in jarosite formation might be released from micas or feldspars. These are commonly found in the parent material of boreal AS soils (Georgala 1980, Öborn 1989, Åström and Björklund 1997). Thirdly, swelling in AS soils might be prevented by Fe and Al oxide coatings (El-Swaify and Emerson 1975), which are commonly found on the surfaces of aggregates and ped faces of ripe AS soils (*e.g.* Dent 1986, Sullivan *et al.* 2012). Brown Fe oxide coatings are frequently mentioned in morphological descriptions of boreal AS soils (*e.g.* Öborn 1989, Joukainen and Yli-Halla 2003).

Depending on the ripening stage in an AS field, the physical soil characteristics commonly vary from one extremity to another within a profile (*e.g.* Joukainen and Yli-Halla 2003, Sohlenius and Öborn 2004, Johnston *et al.* 2009a). When soil dries, the clay platelets form micro-aggregates and simultaneously micropores between the aggregates (Koorevaar *et al.* 1983, p. 22). Then, larger macropores and cracks develop between prisms and blocks. In this process, AS soil sediments with a narrow pore size distribution will be transformed to soils having a wide pore-size distribution with micro- and macropores (Andersson 1955, Johnston *et al.* 2009a). Consequently, in this type of structured soil, a water retention curve (WRC) consisting of two equations also describes the water retention better than a WRC of one equation (Durner 1994, Coppola 2000, Dexter *et al.* 2008).

In AS fields, the response of soil physical properties to the water management is of importance when assessing the leaching of hazardous elements, as well as the impact of run-off peaks on the quality of the recipient waters. When pores and cracks are

continuous, they act as preferential flow pathways (PFP) for water, further assisting the ripening process in soil by allowing the diffusion of oxygen into the soil and by transporting gases to the atmosphere and dissolved reaction products from the soil to recipient waters (Bouma 1988, Cook *et al.* 2004, Johnston *et al.* 2009a).

However, the ripening-induced changes in soils are not self-evidently isotropic, but differ in a horizontal and vertical direction, which affects both preferential water flow and capillary rise (Bouma and Delaat 1981). This renders laboratory-scaled monitoring challenging. For instance, the size of the cores used in sampling may markedly affect the results obtained for the hydraulic conductivity of soil (Anderson and Bouma 1973). Controlling the transport of detrimental reaction products plays a key role in mitigating the off-site environmental hazards of AS soils. However, in boreal conditions, water management, especially waterlogging of cultivated AS soils, has not been explored as an option to restrict the detrimental transport patterns.

1.6. Redox reactions in AS soils

Redox status of soil

Reduction and oxidation reactions (hereafter redox reactions) have direct effects, for instance on the solubility of Fe and S, and also indirect effects via pH, such as on the solubility of Al. Reduction processes result in the formation of sulphidic sediments, and the oxidation of sulphidic material triggers processes leading to on-site and off-site hazards. Therefore, when AS soils are explored, redox processes are in focus. Furthermore, the rehabilitation of AASS soils by waterlogging is based on reduction processes in anaerobic conditions. In other words, the same processes that have formed sulphidic sediments are thought to be able to form sulphides in AASS soils. However, waterlogging alone does not result in reduced soil, as the microbial decomposition of organic matter in the soil is required.

In aerated soil, where molecular oxygen acts as the terminal electron acceptor (TEA) for microbial respiration chain, the availability of electrons is low but increases with an increasing amount of decomposable organic matter. When the oxygen supply is restricted or fully prevented, *e.g.* due to soil waterlogging, facultative aerobic or anaerobic microbes rely on secondary TEAs. They are used according to the thermodynamic sequence of the lowering energy yield gained in the reduction of TEA: the oxidized species of nitrogen, manganese, iron and sulphur, as well as organic acids (Figure 1). However, in soils, the processes may proceed simultaneously or in another order. For instance, the oxidation rate of FeS_2 by Fe^{3+} is kinetically faster than that by aqueous O_2 (Moses *et al.* 1987), and in non-steady conditions the reduction of Fe^{3+} and SO_4^{2-} may occur simultaneously or the reaction order may change (Coleman *et al.* 1993, Postma and Jakobsen 1996).

The soil redox potential (E_h) denotes the abundance of oxidized and reduced compounds in soil, and is the voltage difference between the inert working and a standard hydrogen electrode (SHE). According to the theory of thermodynamics, E_h changes

stepwise, remaining at a given step as long as a given redox-sensitive element is available at an effective concentration, and is thus able to maintain the redox potential at that certain level (Figure 1). This phenomenon, generally termed *poise*, describes the redox capacity of soil. In other words, it means the resistance of a system against redox potential changes upon the addition of a small amount of oxidant or reductant (originally Nightingale 1958, for soils Ponnamperna 1972). Concentrated solutions are generally more poised than dilute ones. In other words, the length of the time step at the given redox level depends on the concentration of the element in question.

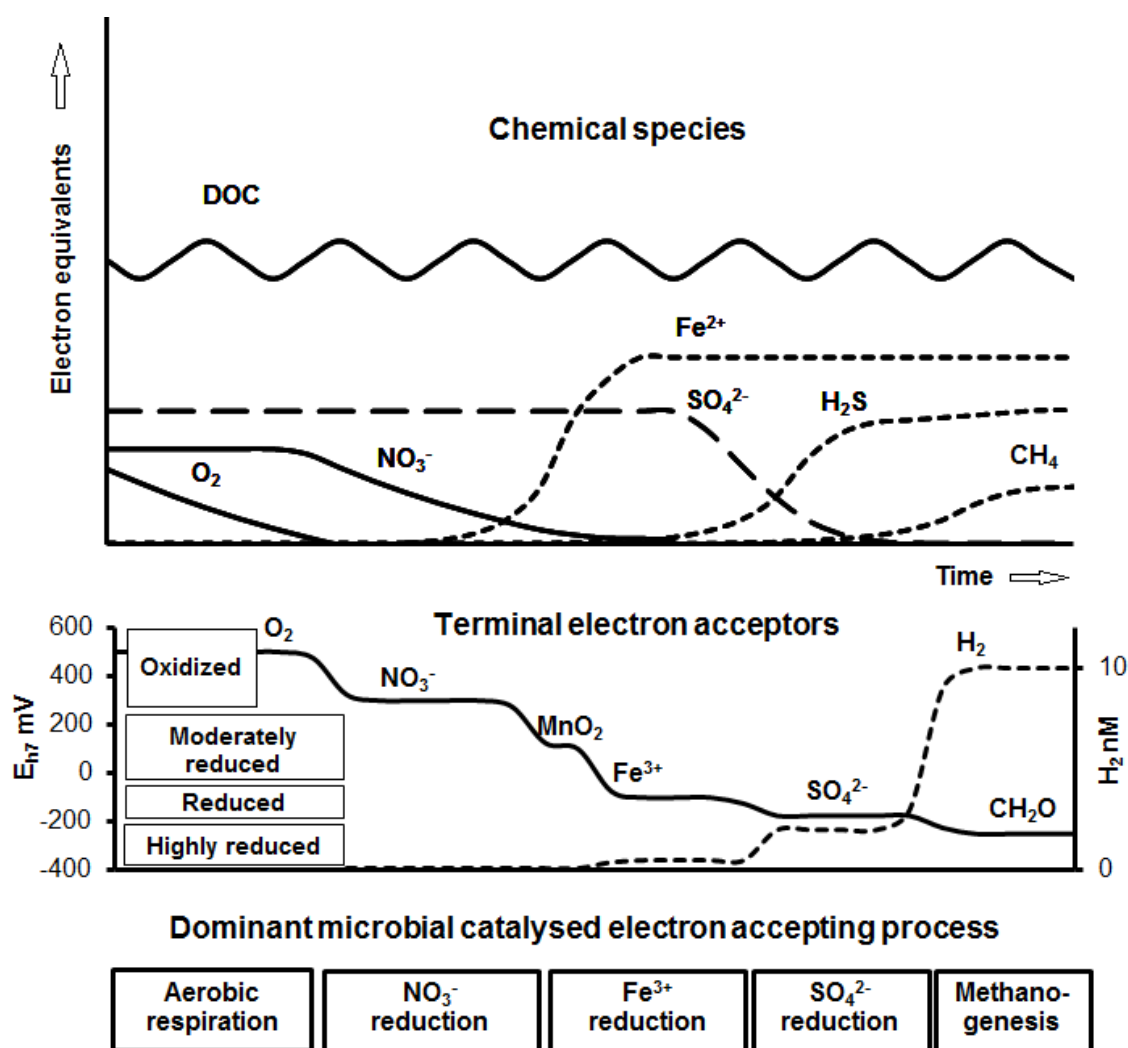


Figure 1. Conceptual model of the decomposition of dissolved organic carbon (DOC) in soils and its sequential impact on soil chemistry and dominating microbially catalysed electron-accepting processes. Modified for the soil system after Wiedemeier et al. (1999). The redox ranges used in this thesis (Paper III) are on the left in the lower figure and refers to the corresponding TEA. The concentration of H₂ refers to the dominant processes in the bottom of the figure.

From the thermodynamic perspective, soil is an open system. No real equilibrium can be attained, because the processes are dynamic. For instance, the continuous addition of electron donors to soil, such as organic compounds, proceeds simultaneously and at different rates with multiple redox reactions, causing a mixed redox potential (*e.g.* Bohn 1971, Lindberg and Runnells 1984). Therefore, the applicability of E_h in the determination of the soil redox status or in the quantification of redox-sensitive elements has been criticized. For instance, in groundwater, where the concentrations of substances are low and E_h is poorly poised, the mixed potential is found to produce misleading results in equilibrium calculations (Lindberg and Runnells 1984).

Consequently, *e.g.* Chapelle *et al.* (1995) proposed that instead of measuring E_h to determine redox processes, the measurement in anoxic soil should be based on H_2 produced by partial fermentation of OM in microbial metabolism. In this approach, the redox status is determined by an electron-donor (H_2) instead of a terminal electron-accepting (TEA) process. This was based on the findings of Lovley and Goodwin (1988) that under steady-state conditions, H_2 is consumed in the thermodynamic sequence of TEA. In other words, the Fe^{3+} reducers consume H_2 first and thus lower its concentration below the level required by the reducers of SO_4^{2-} . Consequently, the reducers of SO_4^{2-} outcompete methanogens (Figure 1), and the partial pressure of H_2 indicates the ongoing process, with threshold values compiled by Kimura and Asakawa (2012). Postma and Jakobsen (1996), in turn, proposed the use of a partial equilibrium approach, where the microbial fermentation of OM is taken as the rate-controlling step and the partial equilibrium is based on the energy yield gained from H_2 . Ultimately, the sequence of TEAs is the same in these two approaches (Figure 1).

In fact, E_h has been used for a long time to characterize the redox status in soil or sediments (*e.g.* ZoBell 1946, Patrick and Mahapatra 1968, Fiedler and Sommer 2004, Fiedler *et al.* 2007). Although this has been criticized, especially in cases of aerated soils (Bartlett and James 1995), in wetland soils and reduced conditions E_h is found to give results that are comparable to the theoretical values obtained in the laboratory (*e.g.* Connell and Patrick 1968, Patrick and Jugsujinda 1992, Fiedler and Sommer 2000, Pan *et al.* 2014) and in fields (Patrick *et al.* 1996, Mansfeldt 2004). Especially when Fe and/or S are present in abundance, E_h is considered to be applicable, because after the redistribution of electrons, the element in excess determines the common potential (Ponnamperuma 1972, Sposito 2008). Because Fe and S play key roles in AS soils, the predominant diagrams or modelling based on E_h were taken to be reasonable in predicting their redox status in this thesis study. Furthermore, when continuous monitoring of E_h by voltage measurements can be arranged, the coupling of the simultaneous monitoring of changes in the soil redox status and elements in soil solution was seen as a promising new option to interpret redox processes.

Redox zones

Classifications of redox environments in soils and sediments are generally based on the thermodynamically defined redox sequence. The redox ranges and zones indicate E_{h7} values controlled by various redox couples and are defined according to the dominant chemical redox reactions (*e.g.* Liu and Narasimhan 1989, Reddy *et al.* 2000, Sposito 2008) or according to reducing microbes depending on the availability of O_2 (Zehnder and Stumm 1988, Reddy *et al.* 2000). They can also be based on an indicator compound such as H_2 (Chapelle *et al.* 1995) or dissolved O_2 and sulphides (Berner 1981). However, the ranges and zones are different when moving from an oxidized to a reduced status than when moving from a reduced to an oxidized status (Patrick and Jugsujinda 1992, Stumm and Morgan 1996). Furthermore, the term redox-cline (Postma *et al.* 1991) and in boreal conditions the chemical drainage depth (the depth at which E_h drops to 0 mV; Palko 1994) have been used to distinguish oxic horizons from anoxic ones.

In field soils, the redox status can be determined by means of qualitative chemical indicators and morphological and sensory observations of the pedon (Bartlett and James 1995), or by quantitative measurement of the depletion of ferrihydrate paint on IRIS tubes (an indicator of the reduction of Fe in soil) (Castenson and Rabenhorst 2006, Rabenhorst 2012).

Soil redox potentials can be expressed at pH 7 using a general conversion factor of -0.059 V/pH (Bohn 1971) or, for instance in the case of $Fe(OH)_3 / Fe^{2+}$, a conversion factor of -0.177 V/pH (*e.g.* Rowell 1981, p. 423, Picek *et al.* 2000). In this thesis, the redox potentials are generally presented at soil pH (E_h). When given at pH 7 (E_{h7}), the general pH conversion factor was used. The redox status of soil is described both according to the redox potential ranges and on the basis of the dominant reduction reaction (see Reddy *et al.* 2000).

2. Objectives of this work

This study was undertaken to unravel the physical and chemical responses of a typical cultivated boreal AS soil to different water management practices and the consequent/concomitant changes in the discharge water quality. While oxidation has been widely studied in boreal AS soils, in this thesis the focus was on reduction and emphasis was particularly given to the waterlogging of AASS horizons and to the consequent redox reactions. As redox processes in soil are markedly microbially catalysed, the prevalence and activity of the microbial community within the soil profile was explored (I). A monolithic lysimeter experiment was conducted to estimate the rates of reduction reactions in different soil horizons in waterlogged conditions (II), and to monitor the effect of different water management systems on chemical and physical properties of the soil (IV), on the chemical composition of pore water (III) and further on the quality of discharge water (IV). The main environmental problems attributable to the AS soils are acid loadings with an excess of Al, which is toxic in aqueous ecosystems. Thus, paper IV of this thesis focuses on water management-induced changes in soil hydraulic properties controlling the transport of Al, Fe and S to watercourses. The practical purpose of this three-scale study was to assess whether the results obtained from monolithic lysimeter experiments could be generalized to the field scale and provide relevant background information for modelling and the planning of mitigation options. Therefore, the similarity of the quality of water collected from monolithic lysimeters to that collected from the parent field was tested (IV).

The working hypotheses of this thesis were that: 1) reduced conditions can be created and maintained in monolithic lysimeters; 2) the permanent soil saturation of AASS horizons results in reduction-induced precipitation of Fe sulphides, which diminishes the leaching of Fe and S; 3) the reduction-induced increase in soil pH results in the hydrolysis of dissolved and exchangeable Al, which lowers the Al concentration in the pore and discharge water; 4) waterlogging does not affect the hydraulic properties of soil created by earlier ripening; and 5) the discharge water quality in a monolithic lysimeter is similar to the field when the water management is the same.

The specific objectives were to:

1. develop a monolithic lysimeter methodology to study the responses of AS soils to water management in controlled conditions (II) and to estimate the possibility to scale up the results from lysimeter studies to the field scale (IV);
2. determine the activity and abundance of microbes in a typical boreal AS soil profile (I);
3. examine the changes in the soil redox potential and redox status and predict the main redox reactions occurring in soil under different water management systems (II, III);
4. estimate the speciation of Fe sulphides in the parent AS field and their changes in AS soil horizons in different water management systems (III, IV);

5. assess the changes in soil hydraulic properties due to different water management systems (IV);
6. monitor the response of discharge water quality to changes in the quality of pore water and estimate the net effect of water management on the acid loading from boreal AS soil (IV, summary).

3. Material and methods

3.1. General description of the study

The data were collected from experiments carried out at soil horizon and lysimeter scales (II) and at the field scale (IV, Figure 2). The field experiment was set up in May 2007, while the lysimeter experiment was established in 2008 after a four-month preliminary experiment with two lysimeters (hereafter referred to as the pre-experiment) in 2007. In the pre-experiment, the methods were developed for the construction of the lysimeters, their sampling and dismantling. At the same time, state-of-art sensors for continuous monitoring of soil physical properties were also tested to confirm that they met the scientific criteria. Furthermore, a systematic pore water extraction procedure, preservation method and analytical methods were tested in order to obtain values comparable on all occasions throughout the lysimeter experiment.

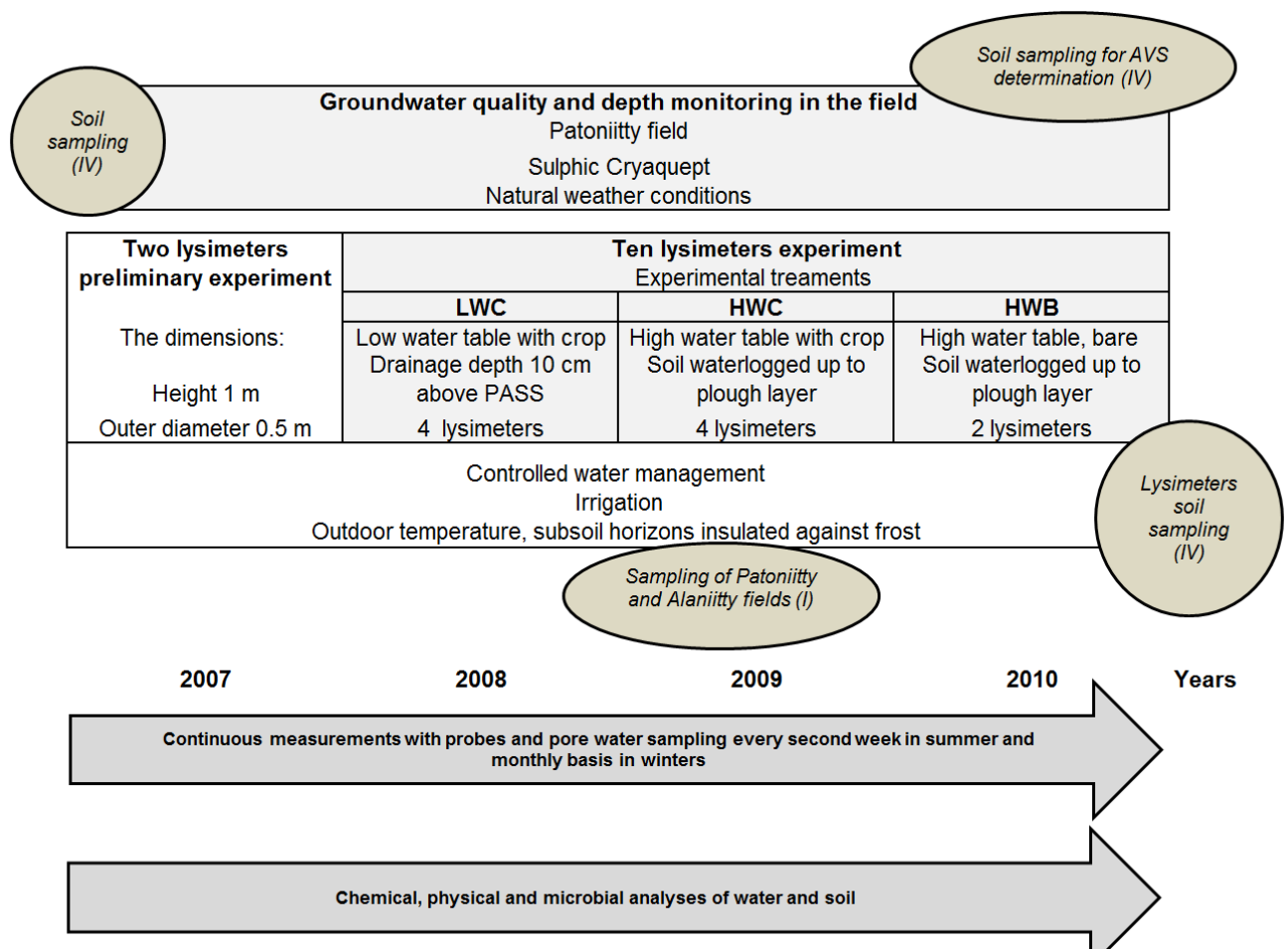


Figure 2. Overview of the experimental setup of the thesis study and the determination of time series variables in the lysimeters and in Patoniitty field (Papers I–IV).

The focus of this thesis study was on the redox reactions in soil, and the redox potential was therefore most frequently monitored in the horizons of the lysimeter soil (II, Appendix A). These data formed a continuous 2.5-year time series from the beginning until the end of the experiment. The pore water and discharge water quality data also formed an equally long time series, but at a lower sampling frequency, varying from the daily to monthly, depending on the season and parameters (III, Appendix A). The third time series consisted of data on the quality and depth of groundwater on the field scale. The collection of this data set lasted one year longer than the time series measurements in the lysimeter experiment (IV). The appropriate chemical and physical properties of the AS soil were determined at the beginning of the study in connection with the excavation of the soil monoliths for the lysimeters, and at the end of the lysimeter experiment (I, II, III and IV, Table 2). In 2009, microbial characteristics in different horizons of the AS soil were determined in the experimental field, as well as in a non-AS field (I, Table 3).

Table 2. *Overview of the measurements of soil chemical and physical properties in Patoniitty field at the beginning of the experiment and in the lysimeter soil at the end of the experiment.*

Paper	Variable	Abbreviation	Unit	Method	Reference
I	pH fresh	pH _{fresh}		ISFET electrode	Soil Survey Staff, 2014
	pH incubated	pH _{inc}			
	Organic carbon	C _{org}	g kg ⁻¹	VarioMax	DIN/ISO 13878
	Total nitrogen	N _{tot}	g kg ⁻¹		
	Total sulphur	S _{tot}	g kg ⁻¹	Aqua regia, ICP-OES	EPA 3051A
	Inorganic nitrogen, NO ₃ ⁻ , NH ₄ ⁺	N _{min} NO ₃ ⁻ , NH ₄ ⁺	g kg ⁻¹		
III	Poorly ordered Fe (hydr)oxides	Fe _o	g kg ⁻¹	Acid ammonium oxalate pH 3, in the dark, ICP-OES	Loeppert and Inskeep, 1996
I, II, III	Redox potential	E _h	mV	Pt probes with Ag/AgCl reference	
IV	Soil water retention curve	WRC		Sandbox Eijkelkamp, 1600 and 1500 Soil Moisture Equipment corp., USA	Dane and Hopmans, 2002
	Saturated hydraulic conductivity	K _s	m hour ⁻¹	Permeameter, Eijkelkamp	Klute and Dirksen, 1986

Table 3. Overview of methods used to determine the microbiological properties of Patoniitty soil (I).

Variable	Abbreviation	Unit	Method
Basal respiration	BS	$\mu\text{g CO}_2\text{-C g}^{-1} \text{ h}^{-1}$	Closed serum bottles, gas chromatography
Substrate induced respiration	SIR	$\mu\text{g CO}_2\text{-C g}^{-1} \text{ h}^{-1}$	Closed serum bottles, gas chromatography
Denitrifying enzyme activity	DEA	$\text{ng N}_2\text{O-N g}^{-1} \text{ h}^{-1}$	Anaerobic slurry, gas chromatography
Dehydrogenase activity	DHA	$\mu\text{g TPF g}^{-1} \text{ h}^{-1}$	Formazan evolution, spectrophotometer
Colony forming unit	CFU	$\text{unit g}^{-1} \text{ dry soil}$	Cultivation, microscopic counting
Culturable cell population density	C	$\text{unit g}^{-1} \text{ dry soil}$	Cultivation, microscopic counting
Total number of bacteria	T	$\text{unit g}^{-1} \text{ dry soil}$	Cultivation, DAPI staining, microscopic counting
Culturable to total cell ratio	C/T		

During the lysimeter experiment (II), the soil horizons were constantly subjected to processes that changed their properties and they were therefore classified according their state at the beginning of experiment. Bg2 and Bgjc horizons were called AASS horizons, because they met the criteria of the thionic horizon. The Cg horizon was termed a PASS horizon, because it contained hypersulphidic material (II). The BCg horizon met the criteria of a thionic horizon (II), but still resembled the Cg horizon in its physical features (IV). Therefore, it was regarded as a transition horizon. The term coefficient of linear extensibility (COLE) was used to describe the irreversible shrinkage properties of soil, although it is actually defined to describe the reversible shrink-swell features in the WRB and Soil Taxonomy (IUSS 2014, Soil Survey Staff 2014).

In addition the elements in the filtered ($<0.45 \mu\text{m}$) water samples were taken to represent dissolved species, although filtrates may contain some particulate matter (Maurice 2012). For simplicity, the total element concentration of soil was defined as the concentration determined by *Aqua regia* microwave digestion (III), even though this method rather describes pseudo-total concentrations (Chen and Ma 2001, Marin *et al.* 2008). Sulphidic material includes sulphides generally separated into three species: Fe disulphides (*e.g.* pyrite, FeS_2), Fe monosulphides (*e.g.* mackinawite, FeS and greigite Fe_3S_4) and elemental sulphur (S_8) (Sullivan *et al.* 2012). Although the operationally defined acid volatile sulphur (AVS) may contain various Fe sulphide species such as FeS and aqueous FeS clusters, and significantly also FeS_2 (Rickard and Morse 2005), the method used in this thesis (IV) mainly comprised FeS (Toivonen 2013). Thus, the general term monosulphides or FeS is interchangeably used with AVS. The general term Fe oxides is used here for Fe hydroxides, oxyhydroxides and oxides, except where more detailed information is needed.

3.2. Experimental work

3.2.1. Study area and soil

The soils investigated in this thesis study were taken from the fields of the research farm of the University of Helsinki (Figure 3). Based on previous studies in these fields (*e.g.* Mokma *et al.* 2000), AS soils were known to occur in the area and their suitability for this study was evaluated beforehand. Soils of the AS field (Patoniitty) (I–IV) and the non-AS field (Alaniitty) (I) had been classified according to their genetic horizons in earlier studies (*e.g.* Mokma *et al.* 2000). The land drainage and cultivation history of Patoniitty field are described in detail in papers I, II, III and IV, and that of Alaniitty in paper I. The soil monoliths of the lysimeter experiment originated in Patoniitty field (I, II, III and IV) and the one-year old reed canary grass (RCG, *Phalaris arundinacea*) turfs planted onto the AS soil monoliths were taken from a non-acid field (Taka-Hakala) (II). The study area is located in the hemiboreal climatic zone and in the cryic soil temperature regime (Yli-Halla and Mokma 1998). In this region, the mean annual air temperature is 5 °C and the mean precipitation is 650 mm (30-year means, 1971–2000; Drebs *et al.* 2002). The mean length of the growing period is 180 days and the duration of permanent snow cover is about 100 days. During the 2.5-year experiment (2008–2010), the air temperature was higher than normal in 2008, close to the long-term average in 2009, and exceptionally high in July 2010 (Korhonen and Haavanlammi 2012). Detailed information on the climatological conditions during the experiment is provided in papers II and IV.

3.2.2. Monitoring in the field

The field scale was the largest one used in this thesis. On Patoniitty field, the groundwater level and the groundwater quality were monitored throughout the experiment. The installation of the monitoring wells and the monitoring of groundwater depth are described in detail in paper IV and the water quality analyses in papers III and IV.

3.2.3. Lysimeter monitoring

Pre-experiment

A pre-experiment was undertaken to develop a method to take AS soil monoliths for the lysimeters to be used in this thesis. Because the AS soil field was at sea level, the deepest horizons were saturated with water and the field had a low bearing capacity and shear strength. For this reason, the use of light PVC cores and sampling with a typical excavator were feasible (II). The original idea to lift the full core vertically out of the soil did not work, because the partly saturated monolith easily dropped from the core back into the pit. However, lifting at an inclined angle was a successful way to pull the lysimeter cores from

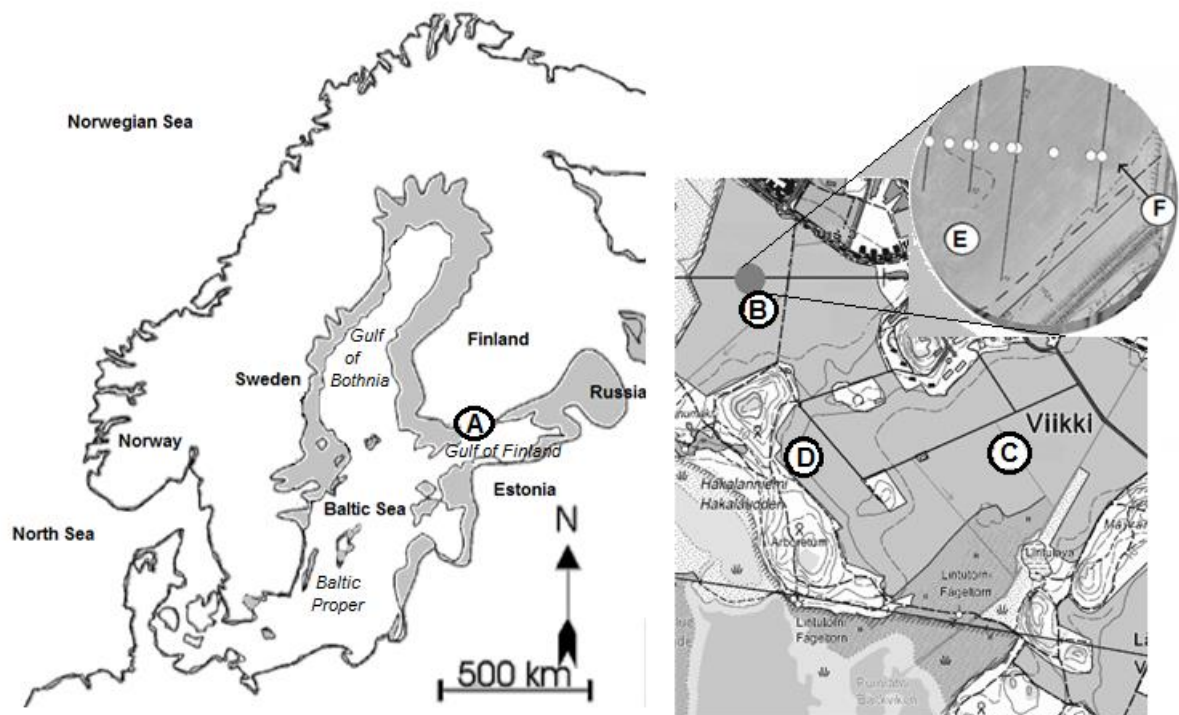


Figure 3. Location of the experimental farm of University of Helsinki (A), Patoniitty (AS soil B), Alaniitty (non-AS soil C) and Taka-Hakala (field where RCG turfs were dug D), the sampling site of monoliths (E) and the groundwater monitoring wells (F) in Patoniitty field. The areas covered by the Litorina Sea on the coast of Baltic Sea are shaded. The map is modified from the original one presented by Westman and Hedenstrom (2002) (Papers I–IV).

the pit. Eventually, the most practical way was to lift the whole core with the excavator bucket. In order to obtain an undisturbed monolith, it was essential to push the core into the soil in an exactly vertical direction. Immediately after sampling, the bottom of the lysimeter was sealed with a PVC cap (II). Due to the practice in the pre-experiment in 2007, the sampling of ten lysimeters took only two days in 2008.

A piston was developed for dismantling of the soil monoliths at the end of the pre-experiment (II). Although the method was extremely simple compared with other techniques (see *e.g.* Reth *et al.* 2007), it functioned well and made the reuse of PVC cores possible. The piston was moved by turning two winches, which facilitated the controlled extrusion of soil with an accuracy of 1 cm (II).

Lysimeter experiment

The lysimeter experiment was located in the same greenhouse compartment with wire-net walls and glass roof where the pre-experiment had been conducted and the functioning of the monitoring system had been tested. A detailed description of the experiment is presented in paper II. The lysimeters were monitored continuously for 2.5 years (II). The response of pore (III) and discharge water (IV) to the treatments was followed at flexible

time intervals so that during the growing season and the periods of heavy rainfall simulations, the water quality was monitored more frequently than outside the growing period (II, III and IV). The sampling intervals and the number of samples are summarized in Appendix A. In the experiment, the impact of permanent waterlogging on soil processes and related changes in soil and drainage water characteristics was studied with four cropped AS soil lysimeters (high water table with crop, HWC) and with two lysimeters without a crop (high water table, bare, HWB). Furthermore, in the four cropped lysimeters, the response of soil and water parameters to efficient drainage (low water table with crop, LWC) was investigated. Unfortunately, one of these had to be discarded because of a malfunction caused by ochre formation (II).

3.2.4. Continuous monitoring of soil conditions in the lysimeters

Soil temperature, moisture and electrical conductivity

In all the lysimeters, temperature (T_m , K), moisture content (ϵ , $\text{m}^3 \text{m}^{-3}$) and electrical conductivity (EC_m , dS m^{-1}) in Ap, Bgjc and BCg horizons were continuously monitored using probes (II). In the preliminary experiment, some corrosion of the gold plating of the probes (ECH₂O-TE, Decagon Devices, Inc., USA) was detected in the most acidic horizons. Therefore, they were replaced by 5TE probes made of stainless steel (Decagon Devices, Inc., USA) (II).

Determination of soil redox potential and soil redox status

In this study, E_h was measured using Pt electrodes (50 self-made redox potential probes, Knuutila *et al.* 2011) and a common Ag/AgCl reference electrode (Inlab 301, Mettler-Toledo, Switzerland) using a saturated KCl salt bridge (Linebarger *et al.* 1975) and data loggers (II). The measurements and the quality control are presented in detail in paper II and in chapter 3.3. In Patoniitty field, the redox potential was manually determined *in situ* in soil pits with a Pt electrode by using a calomel electrode as a reference, and the voltages were measured using a high-resistance voltage meter (III). Redox readings (E_m , mV) were converted to the redox potentials (E_h) relative to SHE by adding 199 mV for the Ag/AgCl electrode and 244 mV for the calomel electrode (equation 1), where f_T was 0.7 (Sawyer and Roberts 1974). The redox potentials at a given soil temperature T_m (K) and soil pH were converted to the redox potentials (E_h) relative to SHE at 298 K (I, II,IV) or further to corresponding values at pH 7 (E_{h7}) using equation 2 (III), where only a general correction factor for pH was used, *i.e.* f_{pH} was 59 mV.

$$E_h = E_m + E_{\text{ref}} + f_T (298 - T_m) \quad (1)$$

$$E_{h7} = E_h - f_{pH} (7 - pH) \quad (2)$$

3.2.5. Pore water sampling

Pore water samples were taken for elemental analysis (Rhizon, MOM, Ø 0.15 µm in porous material, vacuum vials with volume 10 ml) from all horizons every second week in summer, but daily during heavy rainfall events and once a month in winter (see Appendix A and papers III and IV). The pH and EC of the pore water were measured immediately after sampling, whereafter the samples were preserved and stored at +5 °C for chemical analysis (III). Pore water samples for the dissolved organic carbon (DOC) and the total dissolved nitrogen (TN) analyses were also extracted using the same protocol (Rhizon, MOM, Ø 0.15 µm in porous material, PVC syringe, volume 10 ml) on the day following the sampling for elemental analysis, but on a monthly basis. DOC and N samples were stored frozen (-20 °C) until analysis.

3.2.6. Water analyses

Pore, discharge and groundwater samples were analysed for Al, Fe and S, as well as for the major alkali and alkaline earth cations and other selected metals (see Appendix A and the paper III) using an inductively coupled plasma optical emission spectrometer (ICP-OES, Thermo Scientific, ICAP 6000). Chloride was determined coulometrically (Chloride Analyser 926, Sherwood Scientific, UK) from the pore water collected during the heavy rainfall simulations (II). DOC and TN were analysed using the combustion-catalysed oxidation method (TOC-V CPH/CPN, Shimadzu). The analytical methods are described in more detail in papers III and IV. The pore water obtained by extraction was found to approximately represent the water in the drainable pores (IV). The acidity of discharge water (mmol dm^{-3}) was determined according to the standard SFS 3005 by titrating with NaOH to the end point of pH 8.3.

3.2.7. Chemical, physical and microbial analyses of soil

In May 2007, structural soil samples for the determination of hydraulic characteristics (250 cm^3 stainless steel cylinders, Eijkelkamp) and the chemical analyses were collected from one pit dug in Patoniitty field for the soil monoliths used in the preliminary experiment. Both sides of the pit were sampled according to the genetic horizons (Ap, Bg2, Bgjc, BCg and Cg). The same protocol was used in 2008 when taking the grab samples. Additional undisturbed soil core samples were taken from Ap, Bg2, Bgjc and BCg horizons from the pits of ten lysimeters. Furthermore, the same sampling protocol was used at the end of the experiment in 2010 when dismantling the monoliths from the lysimeters (II, IV). The methods for determining K_s and the soil water content (ϵ) in different suction heads for the WRC are described in detail in paper IV and summarized in Table 2. In 2009, for microbial analyses as well as for the determination of the N_{tot} , N_{min} and OC pools of the non-AS and AS soils, large pits were excavated in Alaniitty and Patoniitty fields, respectively (I). In 2010, samples for sulphide analyses were taken as

three replicates to the depth of 2 m from Patoniitty field and analysed simultaneously with the samples taken from the lysimeter soils at the end of the experiment (IV).

Soil sampling, storage and pre-treatment of samples varied according to the analyses. For the determination of N and Fe species, the samples were frozen immediately after sampling and analysed by using just thawed, untouched soil in order to avoid redistribution between the species (Esala 1995, Maher *et al.* 2004, Claff *et al.* 2010). Air-dried soil was used for the total analyses of elements (*aqua regia* digestion, I). The exchangeable cations, cation exchange capacity and poorly ordered Fe oxides (III) were determined by using field moist samples of equal mass on a dry mass basis. The cores taken for the determination of saturated hydraulic conductivity (K_s) and the water retention curve (WRC) were stored (packed in two air-tight plastic bags with a moisturized fabric between them) in the dark at +5 °C. The samples for microbiological properties were stored in plastic bags at +4 °C. In Patoniitty and Alaniitty fields, the soil redox potentials and pH were manually determined *in situ* in the soil pits (I).

3.3. Quality control

The experimental set-up was designed taking into account the quality control of the results. First, the pre-experiment was carried out to avoid irreversible errors in the course of the experiment and to detect the main shortcomings. For example, the water-tight sealing of all joints up to 1 metre pressure was tested.

At the beginning of the field experiment, the inflow rate of water into the wells following their purging was determined. The high hydraulic conductivity of the soil allowed the sampling already after a half-hour time gap. Thereafter, the sampling was carried out systematically in the same way throughout the study period, including groundwater depth measurement, purging of the well and sampling after a half-hour time gap, pH and EC measurements, preservation of samples with ultrapure nitric acid on a volumetric basis, and storage in the dark at +5 °C until analysis. Filtered (syringe filter, 4559 PALL Life Sciences, USA) and unfiltered groundwater samples were taken into acid-washed PE bottles (IV). The blanks (fresh milliQ-water) were sampled and preserved equally with the groundwater samples on every sampling occasion. On a yearly basis, the elevation of the top of the pipe was adjusted to correct the changes caused by ground frost heaving. The pH meter was always calibrated before and at the end of measurements, and its correct functioning was tested down to pH 2.

In the lysimeter experiment, the redox potential from 50 Pt electrodes was monitored by a data logger using two reference electrodes. One reference electrode was coupled to five lysimeter replicates by salt bridges. Each lysimeter was equipped with five Pt electrodes, *i.e.* one Pt electrode was installed per horizon. In other words, in LWC as well as in HWC lysimeters, the total number of electrodes per horizon, was four and in HWB lysimeters two. Fiedler *et al.* (2007) recommended using from five to ten electrodes per horizon. However, in the present study, it was not possible to install this many for

practical reasons. For quality control, the reference electrodes were tested in a standard solution on a weekly basis and the redox readings were occasionally also measured manually. Because the low potentials in soil are easily uncharged, the open circuit and high input impedance proposed, for example, by Rabenhorst *et al.* (2009) was used. Although the Pt electrodes are theoretically inert, their properties may change in long-term use (Austin and Huddleston 1999, Mansfeldt 2003), and the distance between the working and reference electrode may also cause errors (Shoemaker *et al.* 2013). Therefore, in the pre-experiment, the effect of the distance on the readings was checked with and without salt bridges, and it was found to be negligible. The viability of the Pt electrodes in thionic as well as in hypersulphidic soil horizons was also determined by testing them in a standard solution before installation and at the end of experiment (II). The function of 5TE probes was checked in quartz sand before their installation and they were separately calibrated for each horizon (II).

In the lysimeter experiment, pore water sampling as well as analyses and data processing were performed systematically in the same way throughout the experiment. In the sampling, labelled vacuum vials were weighed before and after sampling in order to calculate how much acid should be added and to have the same matrix in all pore water samples preserved (in ultrapure nitric acid solution pH < 2.0). In the sampling, clean needles and acid-washed vials were used and the pore water extraction time (16 hours) was always the same. In the DOC and TN analyses, blanks (fresh milliQ-water) were taken into PVC syringes and stored frozen, like the actual samples.

Owing to the long experimental period, the water samples could not be consecutively analysed by ICP-OES. Thus, for quality control, the known reference samples were included in every run. Furthermore, during the very last run, some water samples from the earlier runs were analysed to assess the between-run differences. Elements were also analysed with multiple wavelengths for quality control. Blanks were analysed, and detection limits were determined systematically in each run according to Greenberg *et al.* (1995). The impurities dissolving from vials and syringes were tested using different acid solutions. Analyses are presented in detail in papers III and IV. In addition, the results were further checked by calculating the charge balance errors (CBE) of major ions in soil solutions, assuming that the elements represented free ionic species (III). Chemical, physical and microbiological analyses of the soil samples were always carried out with two to four replications. The storage time of sensitive samples was minimised. For example, the soil sampling for AVS analyses was not conducted until autumn 2010 in order to have the soil samples analysed at the same time as those from the lysimeters.

3.4. Stability diagrams, chemical modelling and calculation of variables

In order to predict the speciation of the elements in the pore water in the lysimeter horizons, the E_h -pH diagrams (predominance diagrams) were constructed according to Garrels and Christ (1965) and Essington (2003). They are presented in detail in paper III. The activities were predicted by geochemical modelling (PHREEQC-2 developed for Windows, Parkhurst and Appelo 1999) and the effect of temperature was also examined (III). The same geochemical model was also used when predicting the aqueous species of Al, Fe and S in the pore, discharge and groundwater and when assessing the weathering of the most prevalent primary or secondary minerals in boreal non-AS and AS soils (IV). The databases of phreeqc.dat (III) and minteq.v4.dat (III, IV) were used in the modelling simulations. The input files consisted of pH, temperature, E_h and the concentrations of Fe, S and Al, as well as the major elements in the pore water in the given horizons so that, for instance, ionic strength could be taken into account in modelling.

The WRCs were constructed for each soil horizon using a model approach presented by Seki (2007) (IV). The parameters of WRC can be used to visualize the fractions of micro- and macro-pores in soils by depicting the pore size densities (PSD) as a function of equivalent pore radius. According to the method used by Odén (1950) and Durner (1994), among others, the bimodal PSD was depicted on a logarithmic scale, calculating the pore size density using the WRC of a given horizon using equation 3 so that the sum of the pore size densities equalled unity (equation 4) and the difference in the $\log_{10} \psi$ was 0.5. The equivalent pore radius was calculated using equation 5.

$$g(r_i) = w_1 \times \frac{(\varepsilon_{i+1} - \varepsilon_i)}{\varepsilon_s} + w_2 \times \frac{(\varepsilon_{i+1} - \varepsilon_i)}{\varepsilon_s} \quad (3)$$

$$G(r) = \sum_i^k g(r_i) = 1 \quad k = 1, N \quad (4)$$

$$r_i = \frac{0.15}{\Psi_i} \quad (5)$$

$g(r_i)$ = a pore size density for an equivalent pore radius i

$G(r)$ = cumulative pore size density function

r_i = radius of the equivalent pore size in class i , μm , $i = 1, N$

N = number of pore size classes, $N = 12$

Ψ_i = matric suction corresponding to the equivalent radius of a pore size class, cm

ε_s = saturated water content, $\text{m}^3 \text{m}^{-3}$

ε_i = water content at the equivalent radius r_i calculated from the WRC, $\text{m}^3 \text{m}^{-3}$

w_i = the weighting fraction of WRC sub-curves 1 and 2, $\sum w_i = 1$, $i = 1, 2$

Table 4. *Electron equivalents for redox half reactions assumed to occur in the pore water of waterlogged lysimeters.*

Half Reaction	Electron equivalent	Reference
$NO_3^- + 6 H^+ + 5 e^- \rightarrow 1/2 N_2 (g) + 3 H_2O$	$5 * [NO_3^-]$	<i>Stumm and Morgan, 1995</i>
$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2 H_2O$	$2 * [Mn^{2+}]$	<i>Essington, 2004</i>
$Fe(OH)_3(amorp.) + e^- + 3H^+ \rightarrow Fe^{2+} + 3H_2O$	$1 * [Fe^{2+}]$	<i>Lindsay, 1979</i>
$SO_4^{2-} + 10 H^+ + 8 e^- \rightarrow H_2S(g) + 4 H_2O$	$8 * [SO_4^{2-}]$	<i>Stumm and Morgan, 1995</i>

To assess the relative prevalence of various electron donors and acceptors in the waterlogged lysimeters as well as the on-going processes during the experiment, the electron equivalents in pore water and soil redox potential were examined simultaneously. The electron equivalents were calculated by multiplying the number of electrons transferred in the expected redox half reaction by the molar concentration of the corresponding element in the pore water (Table 4) (III).

3.5. Data analysis

3.5.1. Data processing

In the lysimeters, the continuous (every ten minutes) monitoring of soil physical and chemical properties during the 2.5-year period produced a huge amount of data to be analysed (Appendix A). The raw data monitored by data loggers was filtered by discarding erroneous voltage peaks to obtain realistic ranges. The data monitored at ten-minute intervals were then aggregated to hourly and daily means by the data processing environment (SURVO MM 3.21, Mustonen 1992). The soil pH data and the pH, EC and element concentration data collected from the pore water, discharge water and groundwater samples were saved in corresponding data files (*.svo). The files were searched using the MTAB subprogram and the output files were further analysed or depicted using SigmaPlot 12.3 (Systat Software Inc.) or geochemically modelled using PHREEQC.

3.5.2. Statistical analyses

The treatment means were examined using the Student's t-test or, in the case of non-normal distributions, with the Mann-Whitney U-test. The normality of data was inspected by comparing the parameter means and medians, as well as using Shakiro-Wilkinson's test. Because of the non-normal distribution of the data, the relationships between the variables were generally examined by Spearman's rank order correlation coefficients.

Pearson's product moment correlation coefficient was used when examining linear relationships with log-transformed data. The methods are explained in detail in papers I–IV. All statistical calculations were carried out in SigmaPlot 12.3. Generally, the statistical significance was tested at the level $P = 0.05$.

In the figures, the variation in the parameters was illustrated using standard deviations or the standard of errors of the means (I–IV). The temporal variation in the parameters was illustrated by means of box-and-whisker plots for the treatments (III, IV). In the construction of time series, the measured values were used as they were (II, III, IV). On the other hand, moving averages were calculated for the electron equivalent time series to smooth out the random fluctuation in order to more clearly observe the trends. They were calculated by using the average of successive measurements of the element concentrations (two-week moving average) and a 5-day moving average for E_h .

3.5.3. Similarity

The practical aim of the studies on redox processes in boreal AS soil was to produce new knowledge that could be used as relevant background information in the modelling and planning of mitigation options. Although the conditions in the lysimeter experiment appeared to resemble those on the field, the similarity between the lysimeter- and field-scale studies was statistically tested. The approach used to test the similarity is presented by Schuirmann (1987) and by Rita and Ekholm (2007). This test is not commonly used in soil science, but is widely applied in other branches of sciences. The similarity is defined to mean that the parameters are close enough to each other, i.e. within the maximum acceptable difference, the similarity limit (θ_i) being determined *a priori*. In this thesis study, the similarity limit (θ_i) was defined to be the range of the given parameter on the field. The test is explained in detail in paper IV.

4. Results and discussion

4.1. Similarity of the lysimeter experiment with field-scale studies

4.1.1. Chemical quality of pore, discharge and groundwater

The lysimeters served as soil ecosystem models allowing to the examination of processes in AS soils in more detail than in the field. However, as with models in general, lysimeters are simplifications of a real field. Therefore, the results obtained in the studies at three separate scales were compared. In the lysimeter experiment the response patterns of the element concentrations in the discharge water varied greatly between the treatments (IV). The similarity test indicated that the element concentrations in the water discharging from the lysimeters and in the water samples collected in the field were not always commensurable. HWB most closely resembled the field, providing the most reliable evidence for the similarity between the scales. This was because the water regimes in the monoliths originating at the depth of 0.6 m to 1.4 m most resembled those in the field conditions. On the contrary, in the cropped lysimeters, the cultivation of RCG promoted drainage and counteracted waterlogging. In LWC, the roots of RCG penetrated down to the bottom of lysimeters, assisting soil drying and ripening (II). In contrast, in the summer, the high evapotranspiration in HWC made the maintenance of waterlogging challenging. A similar problem has been reported in previous field experiments on the controlled drainage of boreal AS soils (Bärlund *et al.* 2005). However, in the controlled lysimeter conditions, waterlogging could be maintained. The rejection of the similarity hypothesis confirmed that the reaction patterns in HWC and LWC lysimeters clearly differed from those in the Patoniitty field (IV). This outcome emphasizes not only the major impact of water management on the composition of discharge water, but also the dependency of the discharge water quality on soil physical properties, ripening and biological factors.

The processes taking place in various horizons in the lysimeters were reflected in the pore water and affected the quality of discharge water. The comparison of Al and Fe in pore and discharge waters indicated that at the beginning of the heavy rainfall events, the irrigation water mainly flowed through PFPs in the structured upper horizons. In HWB, the linear relationship between pore and discharge waters provided evidence that the water mainly originated from drainable pores (IV). Al and Fe were chosen as indicator metals because of their well-known detrimental impacts on water quality.

4.1.2. Characteristics of AS soil horizons

AASS horizons

The soil of Patoniitty field was classified as *Sulfic Cryaquept* (Mokma *et al.* 2000), which is the most common AS soil type in Finland (Yli-Halla *et al.* 1999). The uppermost acidic

horizons of the field were located from just below the plough layer and extended to a depth of about 1 m (I). The bottom of the transition horizon was only 0.2 m deeper than the drainage depth, because the field was a polder (II). However, it resembled the majority of Finnish AS fields, where the AASS horizons are estimated to reach depths of 1–1.5 m (Yli-Halla *et al.* 2012). The reduced, permanently saturated PASS horizons are found to start at depths greater than 1.5–2.5 m (Joukainen and Yli-Halla 2003, Beucher *et al.* 2013). Generally, the PASS horizons occur deep in the soil profile below the ASS horizons or non-acidic horizons. These contain sediments that are younger than those formed in the Litorina stage or have been covered by peat layers after their emergence from the sea. The fact that the fields have been cultivated for decades or centuries also explains the deep location of PASS horizons.

Up to now, the majority of Finnish fields have been drained by sub-surface drains to depths of 1 - 1.2 m (Äijö and Virtanen 2013). As a result, the upper soil horizons of AS fields have oxidized, depending on the characteristics of the parent sediment, the cultivation and drainage practices (Palko 1994, Österholm 2005, Boman *et al.* 2010) and the length of the period permitting ripening processes (Keso 1940). In non-AS soils, the effect of drainage can be seen even at greater depths than in AS fields (Puustinen *et al.* 1994). In clayey AS soils, the hydraulic conductivity is typically low in PASS horizons and hinders the seepage, groundwater flow and lowering of the water table far below the drainage depth. However, in fine-grained AS fields, the groundwater table is reported to be deeper than 2 m due to the high evapotranspiration enabled by the efficient capillary rise (Joukainen and Yli-Halla 2003, Österholm *et al.* 2015).

Furthermore, the soil profile of Patoniitty field was typical of AS soils, with a concave pH pattern (I) and horizons characterized by Fe oxides on the ped faces and root channels (IV). In particular, the AASS horizons were high in poorly ordered Fe oxides (II, IV), which is typical of boreal conditions (Åström 1998). In the present work, secondary minerals formed due to sulphide oxidation were not identified, but in Patoniitty field, jarosite has been recognized by its colour (Mokma *et al.* 2000) in small amounts. Interestingly, at the end of the experiment, a bright orange mineral was visually observed in the LWC lysimeters (IV, graphical abstract). It was assumed to be lepidocrocite, but not conclusively identified. In Finland, the mineralogy of AS soils has rarely been studied by X-ray diffraction analysis (XRD), but, for instance, jarosite has been identified in the soil of an ASS field (Wu *et al.* 2015) and schwertmannite at mine sites (Bigham *et al.* 1994).

In Patoniitty field, the extremely low pH of the AASS horizon and the very acidic groundwater reveal that the soil has retained its acidic nature, even though it was reclaimed for cultivation and subsurface-drained as early as in the 1950s (I, II, IV). Thus, it represents typical boreal AS fields in which the leaching of hazardous acidic compounds is considered to continue for a long time (Manninen 1972, Österholm and Åström 2004). This is attributable to the retained acidity, for instance in jarosite throughout the AASS horizon and the remaining sulphidic material in the interiors of large prismatic aggregates, in that, in boreal AS soils, sulphides are still present in AASS and transition horizons (Nordmyr *et al.* 2006). Secondary minerals such as schwertmannite or jarosite can store a considerable amount of acidity, which is released in their dissolution and/or conversion to

more stable minerals such as goethite (Sullivan and Bush 2004, data compiled by Sullivan *et al.* 2012). However, the highest amounts of sulphides with potential detrimental environmental consequences exist in the PASS horizons.

PASS horizon

The total sulphur concentration of the PASS horizon is estimated to be roughly equal to the amount of sulphides (Boman 2008, p. 29). On this basis, the PASS horizon of Patoniitty field contained about 2% (w/w) sulphide S (IV), which is slightly higher than the corresponding mean or median in cultivated AS soils in the sediments along the coast of the Gulf of Bothnia in Finland (Purokoski 1959, Sohlenius and Öborn 2004, Boman 2008, Nordmyr *et al.* 2006), and within the range reported in Sweden (Wiklander *et al.* 1950a, Öborn 1989), as well as in warmer climates (data compiled by van Breemen 1973 and Sullivan *et al.* 2012). According to Purokoski (1959), the AS soils on the coast of the Gulf of Bothnia have higher S_{tot} in the plough layer and at the depth of 0.4–0.6 m than fields in the southern Finland. However, on the basis of the present findings, the S_{tot} in the PASS horizon on the coast of the Gulf of Finland appears to be at least within the same range as in the PASS horizon on the coast of the Gulf of Bothnia.

In AS soils, environmental risks are related to the Fe sulphide species. FeS is more reactive than FeS₂ (Wiklander *et al.* 1950b, Bush and Sullivan 1997, Burton *et al.* 2009) and it therefore initiates soil acidification (van Breemen 1973). In Patoniitty field, the PASS horizon was very low in FeS (in the ranges of detection limits, 0.2 mg/g and only about 1% of S_{tot} ; IV), which was indicated by the lack of a black colour in the soil. However, AS soils exceptionally high in FeS have been found on the coast of the Gulf of Bothnia (Georgala 1980, Sohlenius and Öborn 2004), the highest reported content amounting to 88% of S_{tot} (Boman *et al.* 2010). In turn, the AVS concentrations measured on the shorelines of the large lakes in central Sweden (Sohlenius and Öborn 2004) are low, as in Patoniitty field. In this respect boreal AS soils appear to exhibit large variability. Globally, marine AS sediments and sedimentary AS soils are generally low in FeS (van Breemen 1973).

In Patoniitty field, the low FeS content is probably related to the transgression of the Litorina Sea. The rapid rise in the sea level might have converted already partly oxidized FeS to FeS₂ via the polysulphide pathway, as in the upper part of PASS sediments on the coast of the Gulf of Bothnia (see Boman *et al.* 2010). The lamination typically found in the PASS horizons on the coast of the Gulf of Bothnia (Boman *et al.* 2010) has not been detected in the PASS horizon of Patoniitty field (Mokma *et al.* 2000). This suggests that bioturbation on the ancient sea bottom of the region (Haila *et al.* 1991) might also have led to the formation of secondary FeS₂ and, consequently, to the depletion of FeS. Currently, this reaction pattern occurs in some areas on the coast of the Gulf of Bothnia (Boman *et al.* 2010). Unfortunately, sulphide species have only been determined in a few locations in boreal conditions, and not in earlier studies in the coastal area of the Gulf of Finland. Thus, it remains unclear how common the sediments poor in FeS are in the area.

In Patoniitty field, large OC and N pools were found in the transition and particularly in the PASS horizons (I). The low C/N ratio in the PASS horizons suggests that they originated in the autochthonous biomass production in the eutrophic Litorina Sea (Sohlenius *et al.* 1996, Westman and Hedenstrom 2002). The inorganic N mainly occurred as NH_4^+ and its amount was considerable compared to non-AS mineral soils (I). In PASS horizons, OC and N pools might be preserved as a result of the slow decomposition processes under anoxic conditions at low temperatures (I). However, when oxygen penetrates into the Cg horizon, the OC and N pools evidently become more accessible to aerobic or facultative aerobic microbes (I). In LWC, this phenomenon, together with the penetration of RCG into this layer (Epie *et al.* 2014), could also explain the increase in DOC in the pore water (III). Previous studies in boreal AS soils have also reported high OC (Joukainen and Yli-Halla 2003, Paasonen-Kivekäs and Yli-Halla 2005) and N (Paasonen-Kivekäs and Yli-Halla 2005) pools in the PASS horizon, which appear to be typical of boreal AS soils.

4.1.3. Factors controlling redox processes in boreal AS soils

Soil temperature

The redox reactions are strongly microbiologically catalysed. Therefore, temperature is a factor that significantly controls the reaction rates and, consequently, the acid loading from AS soils as well as its prevention by means of reduction reactions. In Finland, the temperature in surface soil undergoes large seasonal variations according to the air temperature, whereas in the deeper horizons, the impact of air temperature is smoothened and lagged (Heikinheimo and Fougstedt 1992) (Figure 4). In addition, in winters the snow cover efficiently isolates soil against frost. Therefore, the common approach of predicting the soil temperature on the basis of the air temperature is not practicable (Yli-Halla and Mokma 1998).

Finnish mineral soils (including AS soils) are reported to belong to the cryic temperature regime, bordering the frigid regime (Yli-Halla and Mokma 1998). In Sweden, the soils on the coast of the Gulf of Bothnia are classified as cryic, and in southern Sweden the temperature regime varies from frigid to mesic (Öborn, 1989). On the contrary, most of the recent studies on waterlogging of the coastal oceanic AS soils have been conducted in warmer temperature regimes, such as thermic or isohyperthermic regimes (*e.g.* Burton *et al.* 2011, Johnston *et al.* 2014) according to the soil temperature regime map (USDA 2003).

The lysimeters used in this study were located outdoors, where the air temperature was practically the same as on the field (II). The temperature of the topmost soil layer in the lysimeter corresponded to the long-term mean (II). In winters, the mean soil temperatures in the lysimeters were similar to those on the field in all horizons (II). However, the exceptionally warm periods in the summers of 2009 and 2010 resulted in soil temperatures above the average. Consequently, soil temperatures in the lysimeters

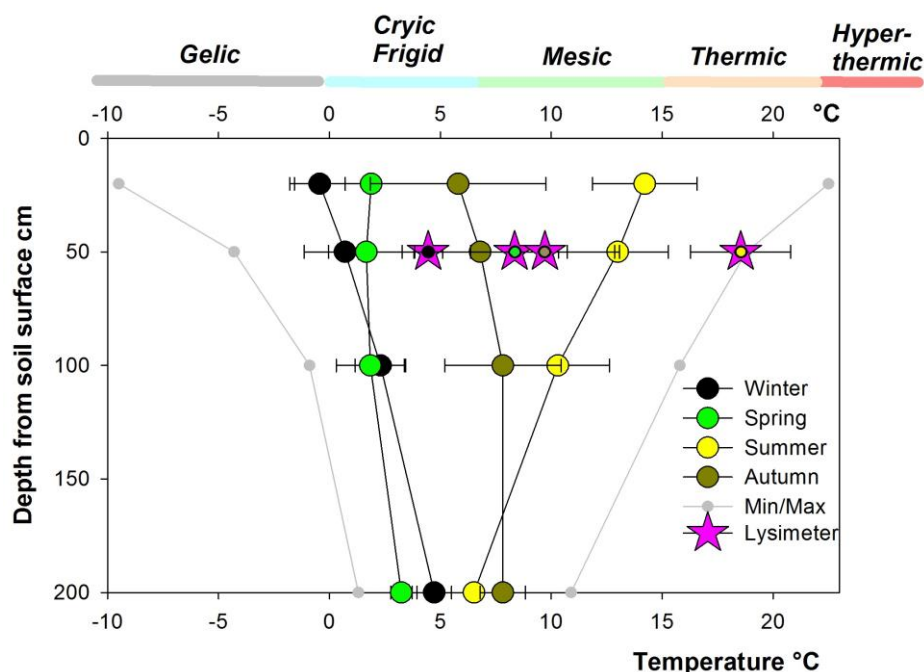


Figure 4. The mean seasonal temperatures in lysimeter soils at the depth of 50 cm during the period 1.8.2008 to 30.9.2010. The mean seasonal soil temperatures at the soil depths of 20, 50, 100 and 200 cm in Finland in 1971–1990 at five locations representing AS soil areas (Heikinheimo and Fougstedt, 1992) (mean \pm standard deviation, minimum and maximum temperatures). The soil temperature regimes based on the mean annual temperature at the depth of 50 cm (Soil Survey Staff, 2014) are presented above the graph. Seasons: winter (1.12.–28.2.), spring (1.3.–31.5.), summer (1.6.–31.8.) and autumn (1.9.–30.11.) (Paper II).

resembled more the frigid than the cryic soil temperature regime. Thus, in terms of soil temperature, the lysimeters gave a good, albeit slightly warmer platform to study the redox processes in boreal AS fields. However, it is argued that the estimated global climate change might turn some of the Finnish soils from cryic to frigid (Yli-Halla and Mokma 1998). This makes the results of this thesis even more representative of field conditions in the future.

Microbial communities in boreal AS soils

In cultivated AS soils, the fate of elements is strongly affected by the microbiota, because the rate of redox reactions is markedly enhanced when catalysed microbiologically. Interestingly, when the soil samples from the PASS horizon were taken into aerobic conditions, they displayed an exceptionally high microbial activity exceeding that in the plough layer (I). This is unusual, because in cultivated fields the microbial biomass and activity are commonly highest in the plough layer and decrease with increasing depth. However, in Patoniitty field this pattern is reasonable, because the PASS horizons had large OC and N pools (see chapter 4.1.2. and paper I). When exposed to oxygen, they can

maintain high aerobic/facultative aerobic microbial activity. A closer examination revealed that in their virgin state, these horizons were enriched with anaerobic microbes, *e.g.* SO_4^{2-} reducers, and were also relatively rich in Archaea (Šimek *et al.* 2014). Recently, anaerobic microorganisms typical of anaerobic and cold conditions have also been identified in the PASS horizon of an AS field on the coast of the Gulf of Bothnia (Wu *et al.* 2013).

In Patoniitty field, the aeration status of the transition horizon BCg fluctuated according to the seasonal variation in the groundwater level (IV). Evidently, these conditions were favourable for facultative anaerobic microbes such as denitrifying microbes. In fact, the denitrifying enzyme activity (DEA) was relatively high in BCg horizon, whereas in AASS and PASS horizons it was low (I). Furthermore, the microbial activity and the number of culturable cells were lowest in the AASS horizons. This distribution pattern was clearly attributable to the low pH and high concentrations of toxic Al in pore water (I, III). Psychrophilic microbes adapted to acid conditions have recently been identified in AASS soil horizons on the coast of the Gulf of Bothnia (Wu *et al.* 2013).

In boreal areas, the annual mean soil temperature at a depth of 0.2–2.0 m is only 4.4–6.4 °C (see Figure 4), i.e. close to the biological zero (see comprehensive review of its definition by Rabenhorst 2005, Soil Survey Staff 2014). Thus, it is evident that mesophilic microbes are relatively inactive and outcompeted by psychrotolerant and psychrophilic species in deep soil horizons, and also in the upper soil horizons. The reduction of $\text{Fe}(\text{OH})_3$ continues at a temperature as low as 2 °C (Rabenhorst and Castenson 2005), and exothermic Fe sulphide oxidation down to zero (Elberling *et al.* 2000). In summers, the higher mean soil temperature, ranging in Finland from 5 to 15 °C depending on the depth (Figure 4), arguably enhances the microbial activity and redox reactions.

4.2. Response of soil physical properties to water management

The AASS horizons in Patoniitty field had a strongly developed structure in the Ap and B horizons (I and IV), and therefore also a wide pore-size distribution and high saturated hydraulic conductivity down to 1 m. On the contrary, the massive PASS horizon below 1.3 m had a very strong shrinkage tendency upon drying, but an extremely low saturated hydraulic conductivity (IV). The same features have been found in AS soils in Sweden (gyttja soils, Andersson 1955) and also in AS soils worldwide (see data compiled by Sullivan *et al.* 2012).

In the HWC lysimeters, the response of soil physical properties to waterlogging was not marked, but some transformations could be observed. The saturated hydraulic conductivity slightly decreased and the water retention capacity increased, but not significantly (IV). However, in HWC the proportion of macropores appeared to slightly decrease, especially in the Bg2 horizon (Figure 5, and IV). In HWC lysimeters, water was available for RCG in the plough layer and the root density was consequently highest in the

Ap and Bg2 horizons (Epie *et al.* 2014). The expansive growth of RCG evidently increased OM in soil (Epie *et al.* 2014), which further assisted the increase in the water retention capacity, as similarly reported by *e.g.* Pons and Zonneveld (1965) and Rawls *et al.* (2003).

Contrary to waterlogging, improved drainage in LWC lysimeters resulted in marked changes in the physical properties of the soils during the 2.5-year experimental period (IV). The RCG grew well, regardless of the extremely high Al concentration in pore water (III). Actually, during the summers, the transpiration by RCG was so high that in all layers above the drainage depth the water content was lower than that obtained by drainage (II, IV). This phenomenon, in turn, forced RCG to extend the roots to the deeper moist soil layers. Actually, in LWC, the roots of RCG almost had double the biomass compared to HWC (Epie *et al.* 2014). Therefore, in LWC, the soil ripening increased the proportion of macropores (Figure 5, IV) and, consequently, the saturated hydraulic conductivity (IV). This response is consistent with the findings of Dent (1986) that in clayey mud soils, the ripening not only proceeds by drainage, but the extraction of water by roots is also needed. These findings indicate that the roots of RCG will not reach deep soil horizons without lowering of the water table. Thus, in lysimeters, drainage and the growth and root elongation of RCG were closely related to each other. In LWC, during the 2.5-year experimental period, the ripening proceeded extensively, supporting observations that the pedogenic processes are extraordinarily rapid in AS soils (van Breemen and Buurman 2002, p. 7). Drying-induced crack formation was recorded by Keso (1940) in field experiments on drainage spacing and depth. In these early studies, better drainage changed the AS soil from a massive to a structured soil at the rate of 23 cm in ten years.

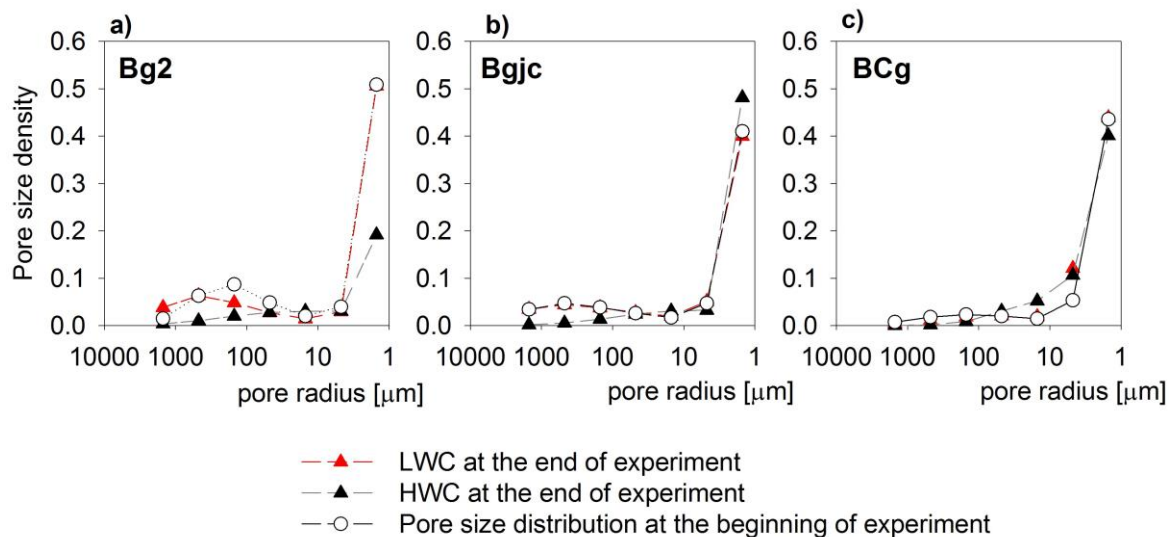


Figure 5. Pore size densities as a function of the pore radius in the lysimeter soils at the beginning and at the end of the experiment a) in Bg2, b) Bgjc, and c) BCg horizons. The treatments presented are the cropped high water table lysimeters (HWC) and the cropped low water table lysimeters (LWC) (Paper IV).

4.3. Redox reactions in boreal AS soils

4.3.1. Response of soil redox potential to water management in lysimeters

In the lysimeter experiment, the E_h of horizons differed distinctly according to the water management practice (II). In LWC, the initially moderately reduced and reduced soil horizons were converted into oxidized ones, except in the winter, when moderately reduced conditions were restored by means of an elevated water table (II). However, in the spring, when the water table was lowered to the BCg horizon, E_h increased in all AASS horizons as well as in the BCg horizon (II). In the Cg horizon of LWC, E_h values peaked in the summer and with a higher frequency in the second and third summer than in the first one (III), indicating that oxidation was proceeding in the subsoil.

The HWC lysimeters were regularly irrigated in order to keep them waterlogged, but the high rate of evapotranspiration (Epie *et al.*, 2014) caused intermittent water unsaturation in the Ap horizon and high daily variation in the redox potential (II). However, in the Bg2 horizon, E_h dropped some weeks after the permanent water saturation from oxidized to moderately reduced, indicating oxygen depletion in the soil. In HWC, the elevated DOC in the Bgjc horizon revealed that some DOC released from the root biomass of RCG had been transported from the Bg2 horizon (III). Consequently, in HWC, the soil horizons were higher in electron donors than the corresponding horizons in HWB. In the Bgjc horizon, in turn, soil reduction from moderately reduced to reduced took about one year. Peculiarly, E_h increased in the winter in HWB (II). This response can be attributed to the cold irrigation water used in the autumn, as well as to the thaw water being higher in dissolved oxygen than the water used in irrigation during warm periods.

The variation in E_h was larger in HWB lysimeters than in HWC lysimeters (III), even though they were both continuously saturated by water (II). This might be related to the lower Fe concentration in pore water and consequently lower poise. In the Cg horizon, E_h remained rather stable throughout the experiment in HWC and HWB (II). The drop in E_h after waterlogging has been documented in laboratory and field studies. However, in the present lysimeter study, the time lag was longer than in studies in warmer conditions (*e.g.* Ponnampersuma 1985, Burton *et al.* 2008). The longer lag time in the present study can be attributed to the relatively low temperature. This increases the solubility of gaseous oxygen, but simultaneously reduces the microbial activity (*e.g.* Tsutsuki and Ponnampersuma 1987, Rabenhorst and Castenson 2005).

4.3.2. Redox-induced changes in soil pH

The soil material of AASS horizons in the present study was initially extremely acidic (I, II). In HWC, a slowly rising trend in pH was observed after waterlogging of these horizons. The increase was highest in the most acidic horizons, Bg2 and Bgjc, but in the Bg2 horizon the pH fluctuated more than in Bgjc (II). In both horizons, a temporary increase in pH was seen in the summers (II). In contrast, in HWB, the rise in pH was only

slight. In the Cg horizons of HWC, the pH approximately remained at the initial values (~ 6), but in LWC the variation was high. The pH fluctuated and temporarily decreased below 5 in the summers of 2009 and 2010, but returned to a higher level during the winter (II). In HWC, an inverse relationship between pH and E_h was clearly seen (Figure 6).

Regardless of the permanent water saturation and decrease in E_h in AASS horizons, the pH slowly increased and a circumneutral pH was not reached (II, III). This outcome was surprising, because reduction reactions generally elevate pH concomitantly with a decrease in E_h (e.g. Ponnamperna 1985, Burton *et al.* 2008). In laboratory experiments, the soil pH has transformed from acidic to circumneutral in some weeks (e.g. Ponnamperna 1972, Burton *et al.* 2008). Johnston *et al.* (2012) reported that the tidal waterlogging of coastal AS plains in Australia elevated the pH by 2–3 units to a mean pH of 6 in 5 years. The marine water significantly assisted the pH rise, because when using freshwater the corresponding increase in pH took 8–9 years in their other field experiment (Johnston *et al.* 2014).

In the present lysimeter study, the sluggish pH rise as response to waterlogging might be attributable to the use of freshwater of low buffering capacity, but also to the acidity retained in the form of exchangeable Al and to secondary minerals formed in the oxidation of Fe sulphides (I, II, III, IV). These secondary minerals in Patoniitty soil have not been identified, but at least the colour of jarosite ($KFe_3(SO_4)_2(OH)_6$) in Bgjc horizons has been documented (Mokma *et al.* 2000). Because jarosite has a concave dissolution pattern, with

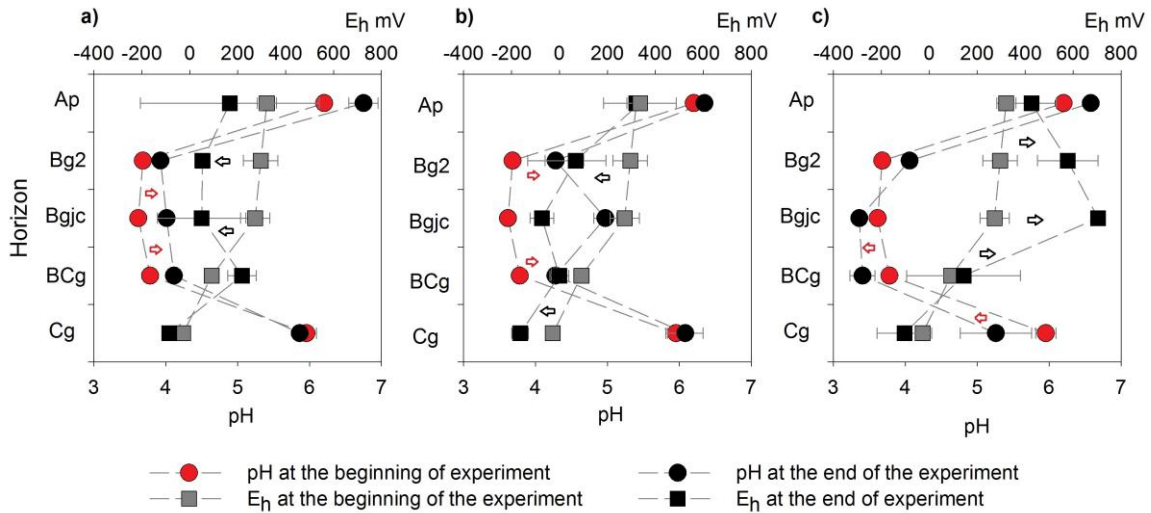


Figure 6. The E_h (mV) and soil pH at the beginning and the end of the lysimeter experiment in different soil horizons in a) the bare high water table lysimeters (HWB), b) the cropped high water table lysimeters (HWC) and c) the cropped low water table lysimeters (LWC) (Paper II). Error bars represent the standard errors of the means and the arrows denote the direction of the change.

the minimum observed at pH 3.5 (Madden *et al.* 2012), the reduction-induced pH elevation evidently resulted in its incongruent dissolution (see Welch *et al.* 2008). This assumption is supported by the concurrent increase in Fe and S in the pore water of the Bg2 and Bgjc horizons in HWC (III). This reaction pattern, in turn, might counteract the rise in pH (II, III). In warmer environments, the proportion of jarosite is also reported to decrease considerably when conditions in soil change outside of its stability field due to waterlogging of AASS (Johnston *et al.* 2009b). Metastable schwertmannite may be transformed, for instance, to goethite and concomitantly release acidity (Bigham *et al.* 1996), whereas its reductive dissolution consumes protons (Burton *et al.* 2007, Johnston *et al.* 2011). In boreal cultivated AS soils, the fate and amount of these secondary minerals have not been studied, and further investigations are therefore needed to assess their possible contribution to acidification processes.

However, even if changes in pH were gradual, contrasting changes in E_h resulted in marked differences in the calculated predominance of Fe species (Figure 7). At the end of experiment in HWC, the reduced species gained dominance, but on the contrary, in LWC, oxidized species were dominant. In LWC, even the occurrence of dissolved Fe^{3+} appeared to be possible due to the low pH and high E_h . It is noteworthy that in HWB, poorer in DOC, the changes were slight, and only in the Bg2 horizon, the direction of development was the same as in HWC. In HWB, the unsubstantial changes can be taken to be attributable to the absence of plants and root material.

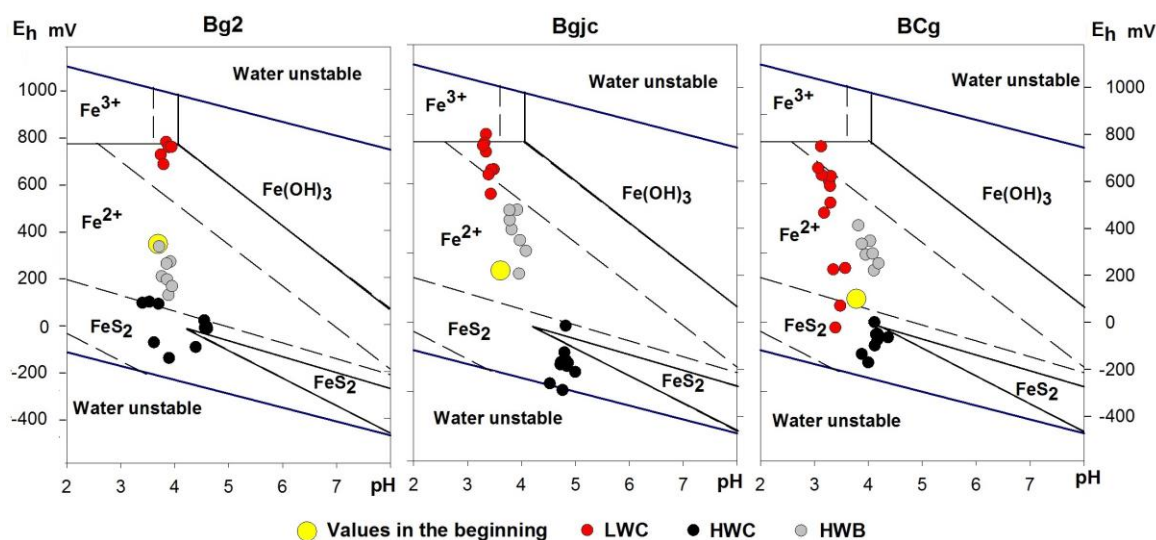


Figure 7. The calculated predominance of selected Fe species in the E_h -pH ranges of Bg2, Bgjc and BCg horizons at the beginning and the end of the lysimeter experiment. The stability areas of pyrite and $Fe(OH)_3(amorp)$ (Lindsay, 1979) are relative to E_h and pH at representative activities of Fe^{2+} (4 mM and 0.2 mM), Fe^{3+} (1 and 0.01 μM), SO_4^{2-} (6 mM and 0.1 mM) and H_2S (6 mM and 0.1 μM) in the pore water at +25 °C. The solid lines indicate minimum and the dashed lines maximum activities calculated from measured Fe and S concentrations using PHREEQC (Paper III).

4.4. Redox reactions related to the water management of cultivated boreal AS soils

4.4.1. Waterlogged soil

Reduction of NO_3^-

In the lysimeter experiment, the electron equivalents of NO_3^- showed their peak values after fertilization (Figures 8 and 9). In AAS horizons of HWB, however, they were regularly higher than those of Fe. An opposite situation was seen in HWC, where NO_3^- was efficiently used by RCG and was consequently not prone to leaching into deeper soil horizons. Actually, the leaching of NO_3^- and its subjection to dissimilatory reduction to NH_4^+ (DNRA) (I), to denitrification and/or to reduction by Fe sulphides (*e.g.* Postma *et al.* 1991, reviewed by Bosch and Meckenstock 2012) can to be taken to explain E_h being higher in HWB than in HWC in the deeper horizons. On the basis of electron equivalents and modelling, Postma *et al.* (1991) proposed the reduction of NO_3^- to be coupled to the oxidation FeS_2 in the redox-cline in a sandy soil aquifer low in OC. Later, the reduction of NO_3^- by FeS was identified in sediments (Schipper and Jørgensen 2002) and by FeS in subsoils high in OC (Vaclavkova *et al.* 2014), as well as by nanoparticulate FeS_2 (Bosch *et al.* 2012). In AAS horizons of HWB, the decrease in the electron equivalent of N seemed to follow the rises in the electron equivalent of Fe (Figure 8), which suggest the reduction of NO_3^- by Fe sulphides to be possible there. Furthermore, in AAS horizons in HWB, the soil redox status was frequently within the range of NO_3^- reduction, which supports the proposed reaction pattern (III). However, this process hardly took place in the Cg horizon of HWB and HWC, even though the electron equivalents of N were higher than that of Fe. The reason for this is that the dissolved inorganic N was mainly in the form of NH_4^+ in the Cg horizon.

In the field, NO_3^- not used by plants or microbes in the upper soil horizons is subjected to leaching. However, when leached rapidly into the deeper soil horizons by heavy rainfall or irrigation, the reduction of NO_3^- may also occur there (*e.g.* Postma *et al.* 1991, Smith *et al.* 1991, Jørgensen *et al.* 2009, Vaclavkova *et al.* 2014). In wet surface soils it can also be lost as N_2O or N_2 by denitrification. In Patoniitty field, the NO_3^- concentration increased as a function of increasing depth down to the transition horizon, where only a negligible amount of NO_3^- was found (I). This outcome suggests that in this horizon, NO_3^- leached from the upper soil layers was denitrified or reduced, for instance by DNRA (I) or Fe sulphides, as found in recent studies. This hypothesis is supported by the finding that the transition layer had the highest denitrification enzyme activity (DEA). Furthermore, it contained NH_4^+ , which in theory can be nitrified to NO_3^- during the temporary aeration in dry seasons and denitrified when anaerobic conditions are restored. Although all these reaction patterns appear to be theoretically possible, further studies are needed to confirm these assumptions.

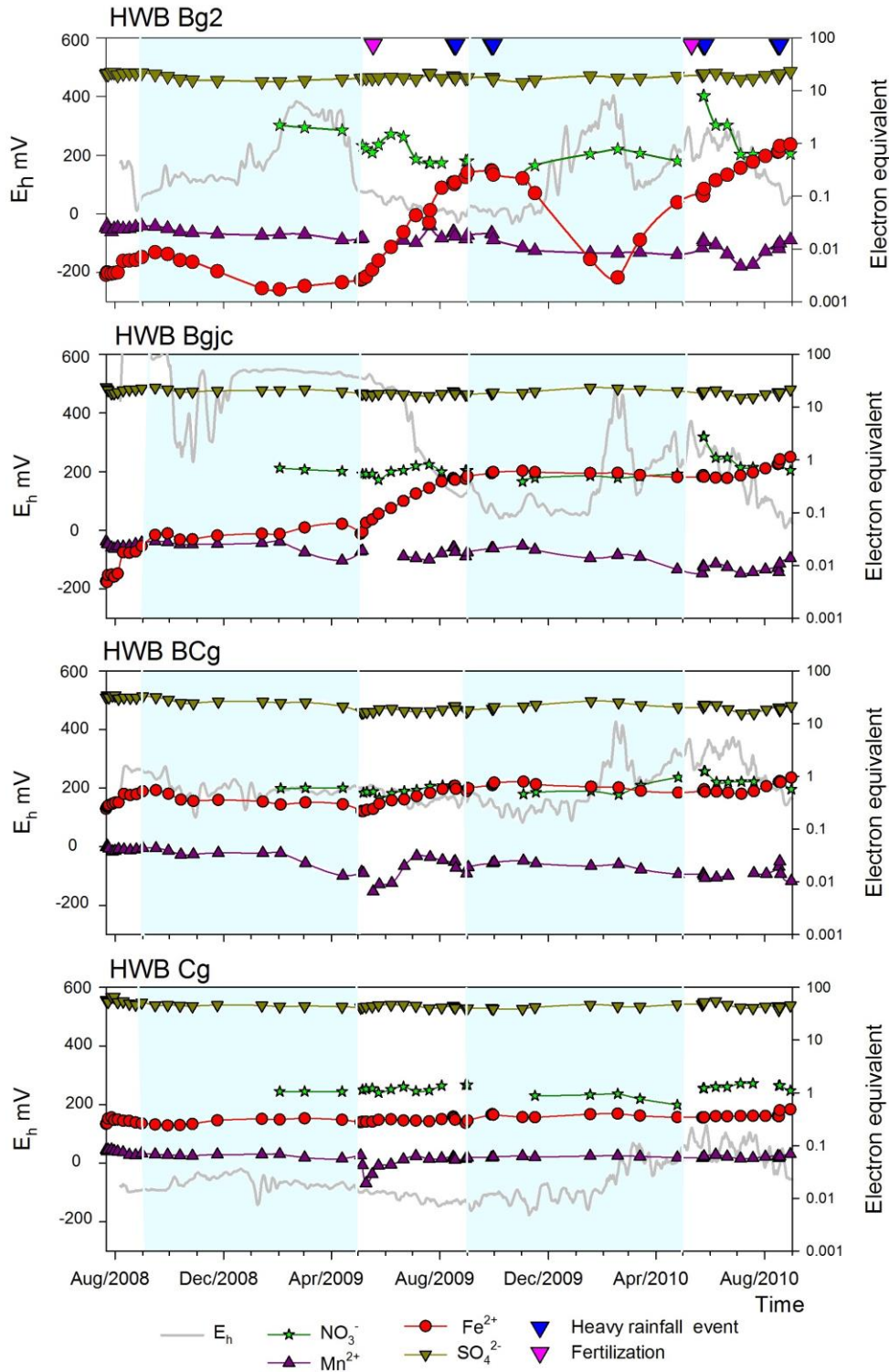


Figure 8. Moving averages of the time series of secondary terminal electron acceptors (TEA) and E_h in the bare high water table lysimeters (HWB) from August 2008 to September 2010 (the data on N are from February 2009 to September 2010) (Papers III and IV). The moving averages for TEA are the mean of two successive measurements and for E_h 5-days mean. The electron equivalents are presented on a logarithmic scale in order to also show the lowest activities.

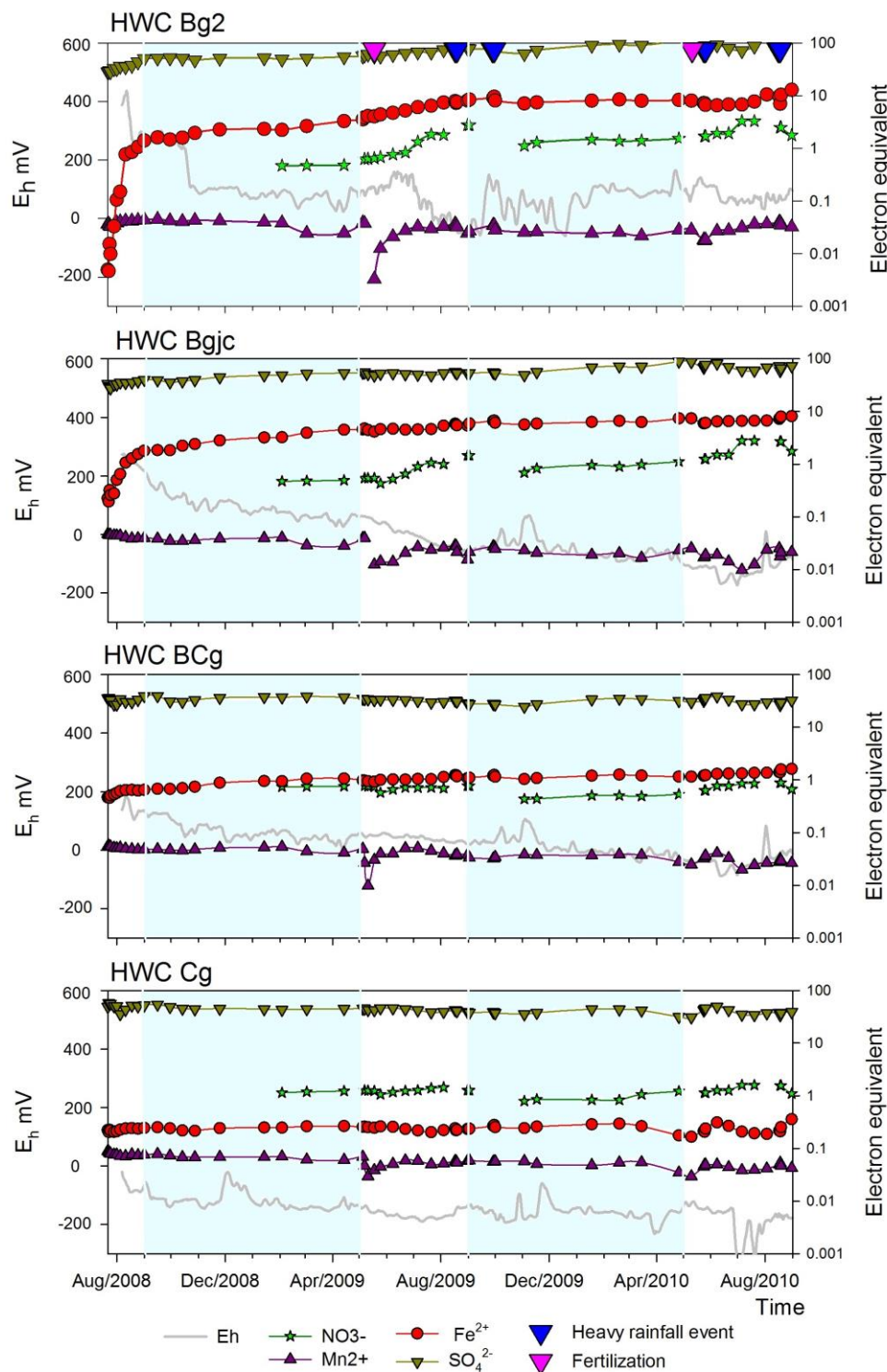


Figure 9. Moving averages of the time series of secondary terminal electron acceptors (TEA) and E_h in the cropped high water table lysimeters (HWC) from August 2008 to September 2010 (the data on N are from February 2009 to September 2010) (Papers III and IV). The moving averages for TEA are the means of two successive measurements and for E_h 5-days mean. The electron equivalents are presented on a logarithmic scale in order to also show the lowest activities.

Reduction of MnO₂

Total Mn concentrations (Mn_{tot}) were low in Patoniitty soil (<0.03% w/w), resembling those in the AS soils on the coast of the Gulf of Bothnia (median < 0.05%, Åström and Björklund 1997) and in B horizons of Finnish cultivated mineral fields (mean Mn_{tot} < 0.05%). Furthermore, the amount of reducible Mn is reported to be on average less than 12% of Mn_{tot} in Finnish cultivated soils (Mäntylähti 1982, p. 425). However, the Litorina Sea sediments deposited below the halocline are found to be higher in Mn_{tot} than the cultivated AS soil (Georgala 1980, Sohlenius and Westman 1998). The AS soil investigated in the present study represent the sediment of a shallow saline/brackish water and therefore Mn has been partly released to water by the reduced conditions (e.g. Stumm and Morgan 1996, p. 907) and later on by acidity (e.g. Öborn 1991, Sohlenius and Öborn 2004), both characteristics increasing Mn solubility. These explain the fact that, the electron equivalents of Mn being a magnitude lower than those of Fe (Figures 8 and 9). It can be concluded that Mn plays a minor role in the redox reactions in this soil.

Reduction of Fe³⁺

In the pore water of HWC lysimeters, the concentration and electron equivalents of Fe increased continuously throughout the experiment (Figure 9), regardless of the Fe losses via leaching (III, IV). Particularly in the Bg2 and Bgjc horizons, this increase coincided with the lowered E_h , which indicates the reduction of Fe³⁺. On the basis of the pH and low E_h , the dominance of Fe²⁺ over Fe³⁺ in pore water was calculated (Figure 7). In HWC, the linear relationship between Fe and DOC in pore water (III) suggests that DOC was the rate-determining factor. It also supports the assumption of the predominance of microbial over chemical Fe³⁺ reduction. Furthermore, in HWB, the Fe concentration was markedly lower and increased more slowly than in HWC (Figure 10), which is in line with the hypothesis of the microbial catalysed reduction of Fe³⁺. Thus, in bare lysimeters, low DOC concentrations delayed the initiation of Fe³⁺ reduction and explained the E_h being higher in HWB than in HWC (II, III). In the Bg2 and Bgjc horizon of HWC, root exudates and organic acids produced by the fermentation of decaying RCG roots might have solubilized Fe³⁺. This reaction might enhance the reduction of Fe³⁺ in soil solution (Lovley 1997). The complexed Fe can be taken to play a minor role in the pore water in HWC lysimeters, where the soil and discharge water were very acidic throughout the experiment (see chapters 4.3.2. and 4.5.1).

In the thermodynamic reduction sequence, Fe³⁺ occurs before SO₄²⁻. However, the reduction of SO₄²⁻ may overlap that of Fe³⁺ (Kirk 2004, Postma and Jakobsen 1996). In soil, this overlapping is attributable to the fact that these oxidants are present in different phases: SO₄²⁻ is dissolved in the pore water whereas Fe³⁺ is mainly bound to the solid phase, except in extremely acid conditions. However, in acidic conditions, the dissimilatory reduction of Fe³⁺ can take place without considerable reduction of SO₄²⁻ (Vile and Wieder 1993, Wendt-Potthoff *et al.* 2010, Kumar *et al.* 2014). This feature is evidently attributed to the optimum pH ranges of microbes. The Fe³⁺ reducing microbes

are rather insensitive to pH, whereas the activity of SO_4^{2-} -reducing bacteria decreases at pH values below 5–6 (*e.g.* comprehensive review of Sheoran *et al.* 2010). In the AASS horizons of the HWC lysimeters, the pH was only temporarily as high as 5.2 (II), which supports the conclusion that Fe-reducing microbes outcompeted SO_4^{2-} reducers.

Furthermore, in the present study, the Bg2 and Bgjc horizons had large pools of ammonium oxalate extractable Fe (see Table 2), *e.g.* poorly ordered Fe-oxide coatings on the ped faces of aggregates and blocks. These are formed as the product of the oxidation of Fe sulphides (III). The reactivity of Fe-oxides towards reductive dissolution depends on their crystallinity, the poorly ordered amorphous forms being the least stable (*e.g.* Postma and Jakobsen 1996). Schwertmannite is found to be reduced over SO_4^{2-} (Burton *et al.* 2007) and, in acidic conditions, also more crystalline Fe oxides (Postma and Jakobsen 1996, Peine *et al.* 2000). At the beginning of the experiment, the Bg2 and Bgjc horizons in HWC were acidic and their pH remained below 5.2 throughout the experiment (see chapter 4.3.2. and paper II). Consequently, poorly ordered Fe oxides and also more crystalline Fe oxides have been subjected to reductive dissolution. However, in reduced conditions with elevated soil solution pH and Fe^{2+} , the transformation of schwertmannite to more stable goethite may occur (Burton *et al.* 2007). Because the source of high dissolved Fe in HWC was theoretically inferred in the present study, the confirmation of these the reaction pathways in boreal AS soils requires further studies, including the identification of Fe oxides by XRD.

In the Cg horizon of HWC, in turn, the circumneutral pH and the soil redox status were favourable for SO_4^{2-} reducers (II, III) identified in that horizon by Šimek *et al.* (2014). In theory, SO_4^{2-} reduction to H_2S can occur not only in the Cg horizon but also in AASS horizons, in bioclusters created by SO_4^{2-} reducers. In these formations the conditions can be more strongly reducing and the pH can be higher than those in the

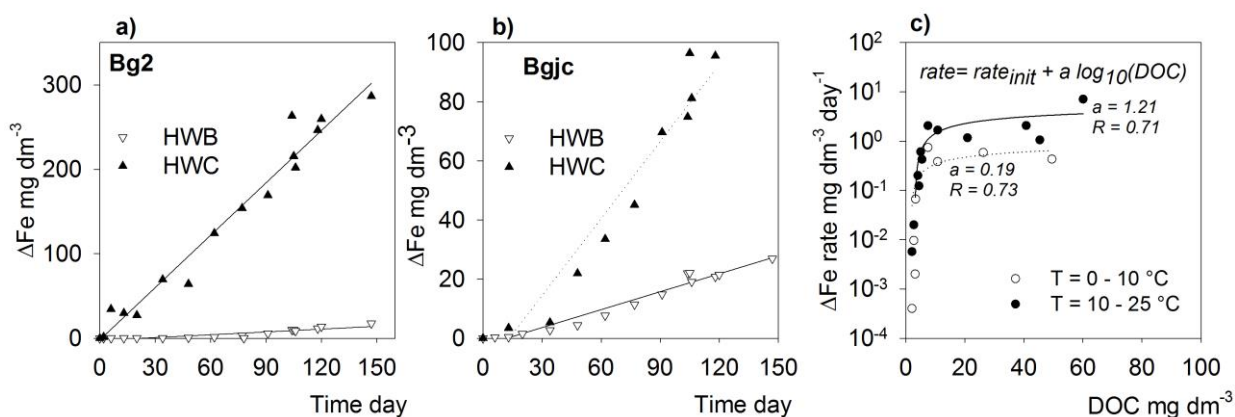


Figure 10. a) The increase in Fe in pore water in the Bg2 horizon of the bare high water table lysimeters (HWB, low DOC) and the cropped high water table lysimeters (HWC, high DOC) in summer 2009 ($T > 10\text{ }^{\circ}\text{C}$), and b) in the Bgjc horizon of HWB and HWC in 2009 and 2008, respectively ($T > 10\text{ }^{\circ}\text{C}$). c) The increase rate of Fe is calculated taking into account the Bg2 and Bgjc horizons of HWB and HWC lysimeters as relative to their DOC concentrations.

surrounding soil (Kirk 2004, p. 142). However, the diffusion of H_2S from the C horizon or the formation of H_2S in the AASS horizons rich in Fe^{2+} would lead to the rapid precipitation of Fe sulphides instead of an increasing concentration of Fe^{2+} in pore water (Table 5, Equation 3).

In addition to the reaction patterns previously proposed, the elevated Fe^{2+} concentrations in Bg2 and Bgjc horizons can be attributable to microbiologically coupled reduction of Fe oxides by NH_4^+ (Table 5, Equations 4 and 5). In anaerobic conditions high in reactive Fe-oxides, this reaction pattern is favoured in an acid environment (Clement *et al.* 2005, Yang *et al.* 2012). In HWC, high transpiration evidently also resulted in an upward flow of NH_4^+ to the reduced Bg2 and Bgjc horizons rich in reactive Fe oxides and labile OC. Therefore, Fe^{3+} reduction coupled to NH_4^+ oxidation is also one possible reason for the high Fe^{2+} concentration in the pore water in the Bg2 and Bgjc horizons. Even though this is theoretically possible, measured evidence is needed to confirm the above in boreal conditions.

At a low temperature, the reduction rate of Fe^{3+} decreased markedly in both the cropped and bare lysimeters (Figure 10c). This agrees with the findings of Vile and Wieder (1993) and Vaughan *et al.* (2009). However, Rabenhorst and Castenson (2005) found that the reduction of $Fe(OH)_3$ will not cease until temperatures decline below +2 °C. This temperature is clearly lower than that in boreal subsoil in winters, wherefore in boreal AS soils the reduction of Fe^{3+} probably continues throughout the year. Even if the microbial catalysed reduction of Fe oxides in HWC can be taken as the most probable pathway leading to elevated Fe^{2+} concentrations in the pore water, further studies are needed to unravel the processes behind these findings.

Table 5. Selected reduction reactions of $Fe(OH)_3$ and $FeOOH$ assumed to occur in boreal AASS fields

Reaction	Equation number
$4 Fe(OH)_3 + CH_2O + 8 H^+ \rightarrow 4 Fe^{2+} + CO_2 + 11 H_2O$	[1] ^a
$16 FeOOH + 8 H_2S + 32 H^+ \rightarrow 16 Fe^{2+} + S_8^0 + 32 H_2O$	[2] ^b
$Fe^{2+} + H_2S \rightarrow FeS + 2H^+$	[3] ^c
$6 FeOOH + NH_4^+ + 10 H^+ \rightarrow 6 Fe^{2+} + NO_2^- + 10 H_2O$	[4] ^d
$6 Fe(OH)_3 + 2NH_4^+ + 10 H^+ \rightarrow 6 Fe^{2+} + N_2 + 18 H_2O$	[5] ^e

^aKirk 2004, ^bPeiffer 2007, ^cRickard 1995 ^dClement *et al.* 2005, ^eYang *et al.* 2012

Reduction of SO_4^{2-}

At the beginning of the lysimeter experiment, the SO_4^{2-} concentrations in the pore water were above the level found to be critical in terms of the reduction rate (<3 mM, Boudreau and Westrich 1984) (III). Thus, some formation of H_2S was theoretically possible. However, while some decrease in SO_4^{2-} concentrations in pore water was detected during heavy rainfall events (III), the SO_4^{2-} concentration in pore water increased in HWC and to some extent also in HWB lysimeters. These outcomes suggest that only the slight formation of H_2S occurred. The elevated SO_4^{2-} concentrations measured in the Bg2 and Bgjc horizons can be partly attributable to intensive uptake of water by RCG (Epie *et al.* 2014), leading to convective S transport from deeper soil horizons or the dissolution of secondary minerals containing SO_4^{2-} (see chapter 4.3.2).

At the end of the lysimeter experiment AVS formation was not practically detected in any of the horizons (IV). However, recent studies in warmer conditions on the waterlogging of AS soils with marine water (Burton *et al.* 2011) or freshwater (Johnston *et al.* 2014) have reported the precipitation of FeS but also marked accumulation of S^0 . In the present lysimeter study, S^0 in soil was not determined. The formation of S^0 is attributable to the oxidation of FeS (Eq. 1, Table 6) or to the reductive dissolution of Fe oxides by H_2S (Eq. 2, Table 5). Neither of the reactions was assumed to occur at a considerable level in this study, but they cannot be totally excluded. Despite the lack of apparent accumulation of Fe sulphides, the reduction of SO_4^{2-} and Fe sulphide formation were theoretically possible in HWC (Figure 7). In acid soils, however, gaseous H_2S can be lost to the atmosphere (Lindsay, 1979, p. 287) or it can be re-oxidized to SO_4^{2-} along its pathway to the atmosphere.

In the present lysimeter study, the soil and/or soil solution pH, temperature and the high concentrations of reactive Fe oxides appeared to have a profound effect on the reduction sequence and explain the contradictory results obtained in waterlogging studies in warmer environments using oceanic water (Johnston *et al.* 2009b, Johnston *et al.* 2012) and freshwater (Johnston *et al.* 2014). In these experiments, waterlogging resulted in the precipitation of Fe sulphides and elevated soil pH. In the present experiment, the non-existence of sulphide precipitation in waterlogged lysimeters was against the working hypotheses. It is, however, reasonable when taking into account that in the AASS horizons, SO_4^{2-} reduction was evidently outcompeted by the other TEAs that were energetically more favourable, such as NO_3^- and Fe^{3+} . Furthermore, in the microbiologically catalysed reactions, the acidity of AAS horizons favours the Fe reducers at the expense of SO_4^{2-} reducers sensitive to acid conditions (*e.g.* Peine *et al.* 2000, reviewed by Blodau 2006). Therefore, the SO_4^{2-} reducers hardly gained dominance, which explains the high Fe concentration in the pore water. Even if the dominance of iron reducers is theoretically possible, further measured evidence is needed.

Methanogenesis

In the waterlogged lysimeters, particularly in the Bgjc and BCg horizons of HWC, the reduction in Fe^{3+} was assumed to be the dominating TEA. However, at the end of the experiment, the soil redox status in these horizons varied between the SO_4^{2-} reduction and methanogenesis zones (III). The theoretical E_h of partial fermentation is lower than that of Fe^{3+} reduction (Zehnder and Stumm 1988, p. 19). Thus, the low E_h in these horizons high in DOC could be attributed to the partial fermentation of the detritus of RCG to form small molecular compounds, such as acetate and fatty acids. These can be further oxidized by Fe reducers

In Patoniitty field, the PASS horizons were very high in OC, which is typical of boreal AS soils (see chapter 4.1.2 and paper I). However, in an earlier incubation experiment carried out on soils taken from Patoniitty field, the methane emissions from AS soil were only of the same order as those from non-AS soil (Šimek *et al.* 2014). This outcome was attributed to the SO_4^{2-} induced inhibition of methanogenesis found to occur in marine sediments (Winfrey and Ward 1983). The PASS horizons in Patoniitty contained some trapped marine SO_4^{2-} , the concentration being close to the threshold value below which methane emissions are reported to increase dramatically (<4 mM, Poffenbarger *et al.* 2011). Thus, emissions were not considerably suppressed by sulphate.

The above proposed redox processes due to water logging in boreal cultivated AS soil low and rich in OM is summarized in figure 11.

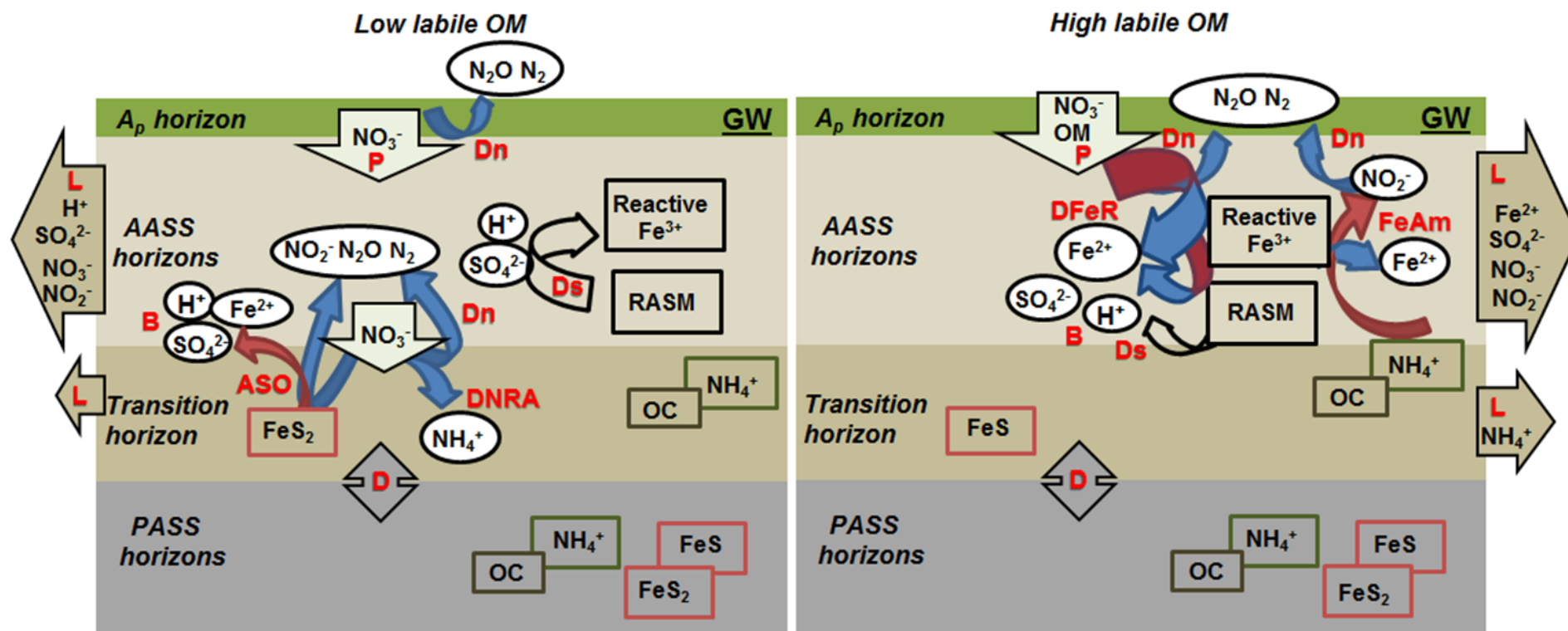


Figure 11. Schematic model of redox processes in boreal AASS soil horizons waterlogged by fresh water that is low (on the left) or rich (on the right) in labile organic matter (OM). Oxidation (in red) and reduction (in blue) are indicated by large arrows, processes in red, soil properties in boxes, the main reaction products in bubbles, and the transport of solution in large arrows (arrow size indicates the rate of flux). GW = groundwater level, ASO = anaerobic sulphides oxidation by NO_3^- , B = soil pH buffering, D = diffusion, Dn = denitrification, DNRA = dissimilatory NO_3^- reduction to NH_4^+ , DFeR = dissimilatory Fe^{3+} reduction to Fe^{2+} , Ds = dissolution, FeAm = NH_4^+ oxidation coupled to Fe^{3+} reduction, L = leaching, P = percolation and RASM = retained acidity in secondary minerals. Oxidation products of organic matter are not presented.

4.4.2 Oxidation of Fe sulphides

Oxidation of Fe sulphides by atmospheric O₂

In Patoniitty field, the PASS horizons were circumneutral and abundant in Fe sulphides (I). However, at the beginning of the lysimeter experiment, Fe sulphides practically consisted of FeS₂ (IV). In HWC and HWB, waterlogging of the Cg horizon efficiently prevented their oxidation by O₂, as indicated by the low E_h being far below oxidized throughout the experiment (II, III). However, in LWC, lowering of the water table elevated E_h in the Cg horizon in two weeks. The redox status turned from reduced to moderately reduced and generally remained at this level, excluding some temporary peaks recorded in summer (II). In the Cg horizon of LWC, pH fluctuated in the course of the experiment and occasionally even decreased below 5. However, it did not drop below 4 (II), which is considered to be a prerequisite for rapid oxidation of FeS₂ by Fe³⁺ (Singer and Stumm 1970). Despite this, the production of acidity already started in the second summer, in 2009, and was further enhanced in the course of time (see chapter 4.5.1).

The transformation from PASS to AASS is generally initiated by the rapid oxidation of reactive FeS by atmospheric O₂ (Wiklander *et al.* 1950b, Bush and Sullivan 1997, Burton *et al.* 2006). This reaction produces Fe²⁺ and S⁰ (Eq. 1, Table 6), but soil acidification does not commence until the oxidation of S⁰ is initiated (Wiklander *et al.* 1950b, Purokoski 1958, Burton *et al.* 2006, Burton *et al.* 2009). However, the laboratory study of Burton *et al.* (2009) on the oxidation of FeS revealed that some microbes also oxidized S⁰ under circumneutral conditions and produced acidity. In the present study, although the Cg horizon of LWC contained only subtle FeS and mainly FeS₂, the oxidation of sulphides already appeared to start in the autumn of 2008. This was indicated by increasing Fe and S concentrations, at first gradually until an abrupt increase was observed at the end of the experiment (III). However, although the mean E_h of Cg horizon in LWC was higher than those of HWC and HWB, it remained below oxidized throughout the experiment (Figure 12). This outcome provides evidence that other TEAs than atmospheric O₂ also oxidized Fe sulphides in the PASS horizon.

Table 6. *Selected aerobic and anaerobic oxidation reactions of FeS and FeS₂ proposed for soils and sediments.*

Reaction	Equation number
$FeS + 1/2 O_2 + H_2O \rightarrow Fe(OH)_2 + S^0$	[1] ^a
$4FeS + 3 O_2 + 6 H_2O \rightarrow Fe(OH)_3 + 4 S^0$	[2] ^b
$2 S^0 + 3 O_2 + 2 H_2O \rightarrow 2 SO_4^{2-} + 4H^+$	[3] ^c
$FeS_2 + 3.25 O_2 + 3.5 H_2O \rightarrow Fe(OH)_3 + 2SO_4^{2-} + 4 H^+$	[4] ^c
$5FeS + 9 NO_3^- + 8 H_2O \rightarrow 5 Fe(OH)_3 + 5 SO_4^{2-} + 4.5 N_2 + H^+$	[5] ^d
$FeS_2 + 3 NO_3^- + 2 H_2O \rightarrow Fe(OH)_3 + 2 SO_4^{2-} + 1.5 N_2 + H^+$	[6] ^d
$FeS + 1.5 MnO_2 + 3 H^+ \rightarrow Fe(OH)_3 + S^0 + 1.5 Mn^{2+}$	[7] ^e
$FeS_2 + 7.5 MnO_2 + 11 H^+ \rightarrow Fe(OH)_3 + 2SO_4^{2-} + 7.5 Mn^{2+} + 4 H_2O$	[8] ^e
$FeS_2 + 14 Fe^{3+} + 8 H_2O \rightarrow 15 Fe^{2+} + 2SO_4^{2-} + 16 H^+$	[9] ^c

^aWiklander 1950b, ^bPurokoski, 1958, p. 52, ^cvan Breemen 1973, ^dSchippers and Jørgensen 2002, ^eSchippers and Jørgensen 2001.

Oxidation of Fe sulphides by NO_3^-

In the second summer of the experiment (2009), the electron equivalent of N in the Cg horizon of LWC was higher than those of Fe and Mn (Figure 12). This indicates that NO_3^- was a preferential oxidizer of Fe sulphides over Fe^{3+} . However, the electron equivalent of N in this layer diminished only temporarily, although it was assumed to be consumed in the oxidation of Fe sulphides. This reaction pattern can be explained by a continuous recharge of NO_3^- . It could be leached from the aerobic topsoil rich in OM and having a high pH (owing to liming) favouring the mineralization of organic N and its subsequent nitrification. The portion of NO_3^- not taken up by plant could have ended up in Cg horizon. Actually a considerable increase of E_h in BCg and especially in Cg horizon (II, Figure 12) refers to the nitrification of abundant NH_4^+ reserves (I). Furthermore, the convection or diffusion of NO_3^- into the circumneutral Cg horizon was not restricted by pH-induced precipitation, as was the movement of Fe^{3+} . In the boreal climate, where annual precipitation exceeds evaporation, NO_3^- also leaches to subsoil *e.g.* in autumns, filling the unsaturated pores emptied by capillary forces in the summer and then further via drainage pipes to watercourses. Therefore, drainage water is typically high in NO_3^- in non-AS fields (Äijö *et al.* 2014) and even higher in AS fields (Uusi-Kämpä *et al.* 2012). Along its flowing pathway, it may cause the oxidation of Fe sulphides in AS fields.

Furthermore, NO_3^- -driven oxidation of Fe sulphides is found to occur in deep soil layers at low temperatures (Eq. 5 and 6, Table 6). Based on groundwater and sediment data, as well as the electron equivalent calculation and modelling, Postma *et al.* (1991)

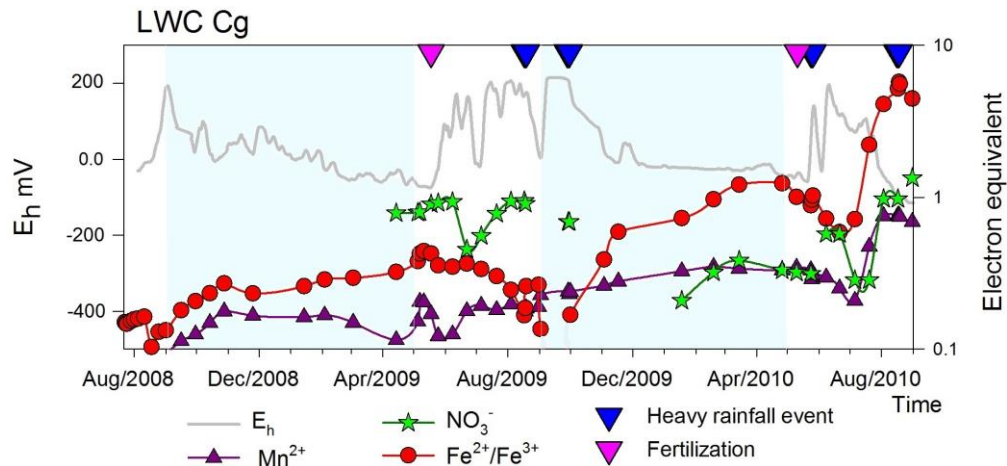


Figure 12. Time series of secondary terminal electron acceptors (TEA) and E_h in the cropped low water table lysimeters (LWC) from August 2008 to September 2010 (the data on N are from April 2009 to September 2010) (Papers II and III). The moving averages of TEAs are the mean of two successive measurements and that of E_h a 5-day mean. The electron equivalents are presented on a logarithmic scale in order to also show the lowest activities.

proposed that pyrite is oxidized by NO_3^- . Subsequently, the oxidation of FeS by NO_3^- in sulphidic sediments has been confirmed in laboratory experiments (e.g. Garcia-Gil and Golterman 1993, Schippers and Jørgensen 2002), as well as the oxidation of FeS_2 by NO_3^- in deep aquifers low in OC (Jørgensen *et al.* 2009), but also in those high in OC (Vaclavkova *et al.* 2014). In the last-mentioned study, it was observed that the reaction pattern might be inhibited in highly saline sediments ($\text{EC} > 13 \text{ mS cm}^{-1}$), but not in soils like the soil in our lysimeters. Furthermore, Fe^{2+} released from Fe sulphides can be oxidized by NO_3^- to Fe^{3+} , subjected to hydrolysis or further cause the oxidation of FeS_2 (e.g. Stumm and Morgan 1996, p. 480, reviewed by Bosch and Meckenstock 2012). Theoretically, the oxidation of Fe sulphides by NO_3^- is possible, but further evidence is needed to unravel the pathways and their significance in boreal AS fields.

Oxidation of Fe sulphides by MnO_2 and Fe^{3+}

The very low Mn_{tot} ($<0.05\%$ w/w) and the Mn electron equivalent being lowest in the Cg horizon of LWC indicates that MnO_2 did not contribute to the oxidation of Fe sulphides. This is consistent with the conclusion by Boman (2008, p. 38) that MnO_2 is not a very important oxidant in AS soils on the coast of the Gulf of Bothnia. The anaerobic oxidation of Fe sulphides by MnO_2 is found in circumneutral marine sediments (Schippers and Jørgensen 2001, Schippers and Jørgensen 2002) (Eq. 7 and 8, Table 6), but their properties decisively differ from those of boreal AS fields.

In the Cg horizon of LWC, the electron equivalent of Fe did not overlap with that of N until the end of 2009, so NO_3^- appears to have been the main oxidizing agent for Fe sulphides (Figure 12). Although Fe^{3+} accelerates the oxidation of Fe sulphides by a factor larger than 10^6 (Singer and Stumm 1970), the decreasing solubility of Fe^{3+} due to the pH rise (Lindsay 1979, p.129) and acidophilic microbes catalysing the oxidation of Fe^{2+} to Fe^{3+} (Arkesteyn 1980) makes this process favourable only at a low pH (<4). In LWC, the initially neutral Cg horizon became slightly acidic, but the extremely acidic conditions were not reached in the course of the experiment (II, Figure 6). Therefore, the acid-releasing loop enhancing the oxidation of FeS_2 was not created. However, Fe sulphides have a tendency to form clusters or nodules in soils (data compiled by Sullivan *et al.* 2012). In this microcosmos, FeS_2 oxidation by Fe^{3+} is possible, if more acidic conditions than in the surrounding soil are created. In LWC, the pore water of Bgjc horizon contained Fe^{3+} according to the calculation (Figure 7). However, Fe^{3+} hardly could leach to Cg horizon due to its tendency to precipitate at the pH of Cg horizon. Therefore, a pH-intolerant mobile oxidant such as NO_3^- was taken to initiate the acid-generating sulphide oxidation loop leading to the coupled microbial oxidation of Fe^{2+} to Fe^{3+} . This reaction pattern would explain the rapid increase in Fe in pore water of the Cg horizon in LWC at the end of the lysimeter experiment (III). These theoretically possible reaction pathways need further studies as well as measured evidence to be confirmed.

The above proposed redox processes in boreal cultivated AS soil during dry and wet periods are summarized in figure 13.

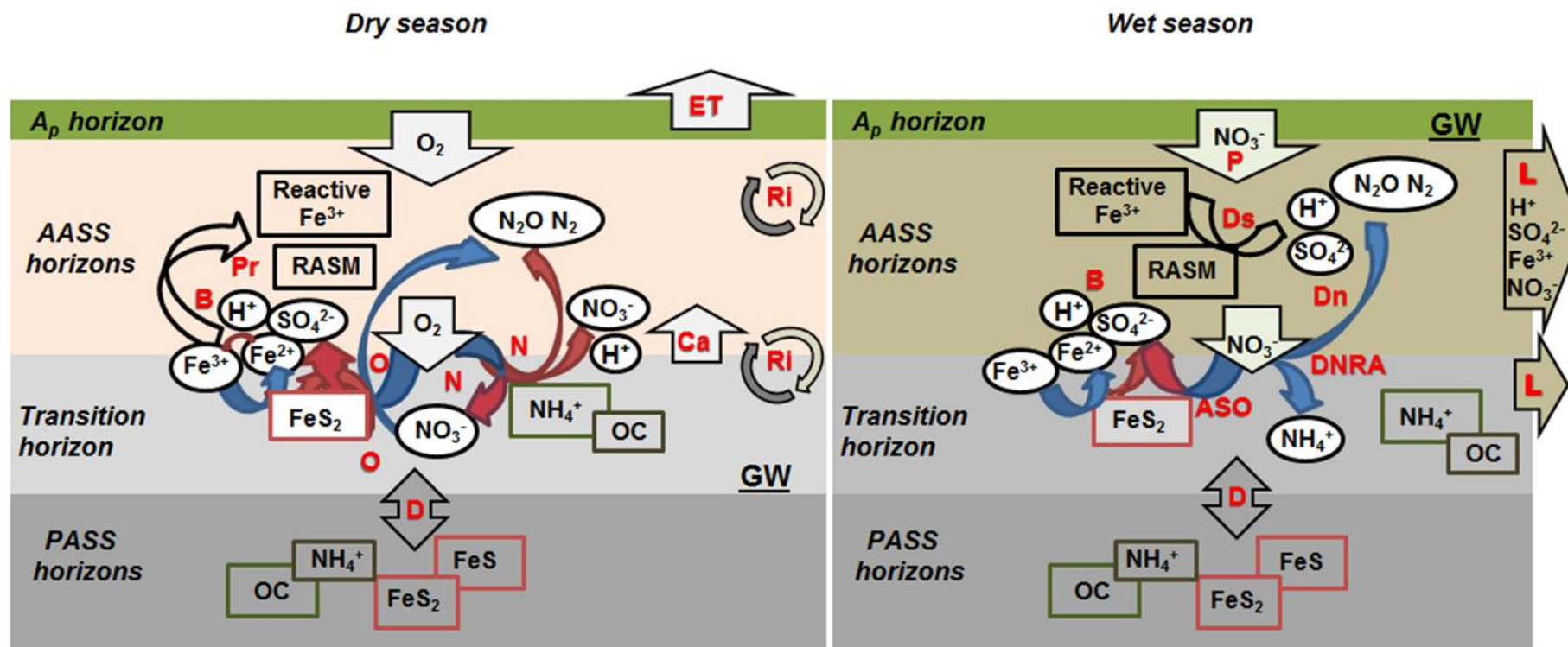


Figure 13. Conceptual model of redox reactions in cultivated boreal AS soil during a dry (on the left) and a wet (on the right) period. Oxidation (in red) and reduction (in blue) are indicated by large arrows, processes are indicated in red, soil properties in boxes, the main reaction products in bubbles, and the transport of solution in large arrows (arrow size indicates the rate of flux). *GW* = groundwater level, ASO = anaerobic oxidation of sulphides, B = soil pH buffering, Ca = capillary rise, ET = evapotranspiration, O = oxidation, DNRA = dissimilatory NO_3^- reduction to NH_4^+ , D = diffusion, Dn = denitrification, Ds = dissolution, L = leaching, N = nitrification, P = percolation, Pr = precipitation, L = leaching, RASM = retained acidity in secondary minerals and Ri = ripening. Reduction products of O_2 are not presented.

4.5. Impact of water management on the quality of discharge water

4.5.1. Acidity

The discharge water from the HWC lysimeter remained extremely acid throughout the experiment, regardless of waterlogging (Figure 14). This was against the working hypothesis, but reasonable when taking into account that waterlogging did not immobilise Fe^{2+} as Fe sulphides (IV). Therefore, the extremely high Fe^{2+} concentration in pore water (II) resulted in acidic discharge water (IV) and partly undermined the positive effect of immobilisation of Al (IV). Hence, the risk that waterlogging of AS soils by freshwater may enhance the leaching of Fe cannot be excluded in the boreal climate.

In boreal conditions, the mean acidity of drainage water is reported to vary from 4 to 18 mmol dm^{-3} (Palko 1988, Bärlund *et al.* 2005). In HWC and LWC, the acidity values were generally in this range. However, the distinct difference between these constraining treatments was that the peaks in the Fe and Al concentrations in pore and discharge water were lacking in HWC (III, IV). Thus, in HWC, the acidity of discharge water did not show any episodic high values (Figure 14). This appeared to be due to the permanent saturation of the Cg horizon (II), which prevented the oxidation of Fe sulphides and the formation of PFP, and thereby prevented outflow peaks. On the contrary, in HWB, waterlogging substantially lowered the Al concentration without marked increase in the Fe concentration (III, IV). This resulted in the lowest mean acidity in discharge waters (mean \pm SEM = $3.3 \pm 0.2 \text{ mmol dm}^{-3}$). In LWC, the acidity loadings significantly increased in the third experimental year. This finding is well in line with a previous Finnish field experiment on AS soils in which virgin PASS soil was drained by using various methods and the highest increase in acidity was observed three years after the drainage (Palko 1994). Despite the different scales of these two experiments and the different soil texture and total sulphur content in PASS horizons, the release of acidity started after a similar time lag from the implementation of efficient drainage.

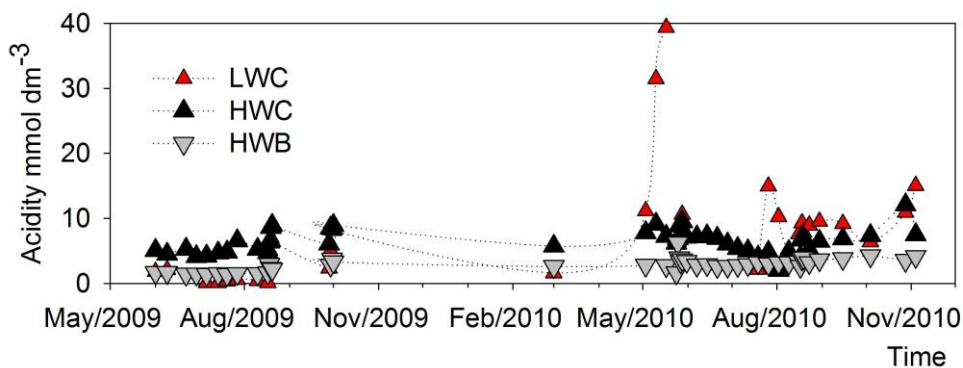


Figure 14. The acidity of discharge water in the cropped low water table lysimeters (LWC), the cropped high water table lysimeters (HWC) and the bare high water table lysimeters (HWB) between May 2009 and the end of October 2010.

4.5.2. Elemental composition

In HWB, and particularly in HWC, the Al concentration in the pore and discharge water decreased to low concentrations (III, IV). Indeed, in HWC, the reduction-induced increase in pH strongly immobilised the pH-dependent Al (II, III, IV). However, reduction reactions increased the concentration of Fe in pore water, not only in HWC but also slightly in HWB. These changes were reflected in the proportions of Al and Fe in discharge water (Figure 15). On the contrary, the intensified drainage in LWC caused notable soil cracking in quite a short time and thus created flowpaths for water and improved the diffusion of air into the soil. In LWC, the initially high Al concentration in the pore water in Bgjc and BCg horizons increased to extremely high level in the course of the experiment (III). This can be taken to be caused by the oxidation of Fe sulphides and consequent sulphuric acid formation (II, III). The upward flow transported protons to the upper horizons, resulting in enhanced weathering (IV). The release of structural Al from the oxides and edges of clay minerals buffered against changes in pore water pH (IV). Therefore, only a slight decrease in pH was observed in the Bgjc and BCg horizons (see chapter 4.3.2 and paper II), even though the Al concentration in pore water markedly increased (III). On the contrary, in the Bg2 horizon, pH actually increased slightly (Figure 6) and the Al concentration decreased in the course of the experiment (III), supposedly due to efficient leaching or precipitation.

A similar pattern was also observed in a laboratory experiment by Hartikainen and Yli-Halla (1986), in which Ca, K, Na and Mg leached from soil in the initial stage of oxidation of PASS material. The leaching of Al did not commence until it saturated the cation exchange sites. In the present study, the exchange sites in AASS horizons of Patoniitty soil, particularly in the Bgjc horizon, were already nearly saturated by Al at the beginning of the experiment (I). Therefore, it can be assumed that weathering of aluminosilicates and secondary Al minerals in LWC further increased Al concentrations in the pore water and, consequently, in the discharge water (III, IV). The reaction pattern recorded in LWC was well in line with those studies in which Al concentrations in watercourses have proven to derive from cultivated AS fields, being attributable to their efficient drainage (*e.g.* Edén *et al.* 1999, Nordmyr *et al.* 2008).

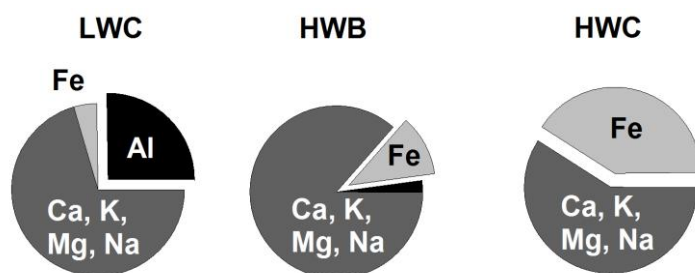


Figure 15. The proportions of Al and Fe in the cation composition (mmol dm^{-3}) of the discharge water from the cropped low water table lysimeters (LWC), the cropped high water table lysimeters (HWC) and the bare high water table lysimeters (HWB) at the end of the experiment in autumn 2010.

4.6. Waterlogging as a method to mitigate the detrimental environmental consequences in cultivated boreal AS soils

Response of water quality to waterlogging

In boreal fields, drainage is typically needed to obtain optimum conditions for plant growth and for cultivation measures. However, in AS fields, it is a controversial measure from the environmental point of view, because it increases the risk of oxidation of hypersulphidic material in PASS horizons. Therefore, RCG, a water-tolerant crop that has recently been cultivated for energy production in the coastal area of the Gulf of Bothnia, was chosen in the present study. The results obtained with RCG in the lysimeters under waterlogging can be taken as also applicable to describe the conditions if cultivated fields are abandoned, waterlogged and colonised by natural reed vegetation.

In the present lysimeter experiment, the proportion of reactive Fe sulphides out of the total sulphides in the PASS horizon was considerably lower than the highest values reported on the coast of the Gulf of Bothnia (Boman *et al.* 2010). Therefore, in the present experiment, the evidence for various oxidation pathways might be less distinct than in AS soils higher in reactive Fe sulphide species. However, in the AS soils on the coast of the Gulf of Bothnia, the amount of reactive Fe sulphides has been found to vary markedly (Toivonen 2013, p. 17), being in some soils as low as in the present study. Furthermore, there is no information on reactive Fe sulphides in soils on the coast of the Gulf of Finland. There, the area of AS soils could be larger than hitherto assumed (Beucher 2015) when also taking into account those located on the Russian coast (Kivinen 1938). Thus, the results are more widely applicable than solely to the region of the present experiment. The waterlogging-induced reduction of ripe AS soil is not connected to Fe sulphide species, which widens the applicability of the findings from the present study in boreal conditions.

Drainage makes the soil structure more permeable via ripening processes, whereas waterlogging prevents soil ripening and restricts the diffusion of O₂ and other TEAs into the soil, and the oxidation of hypersulphidic material consequently ceases. Waterlogging up to the plough layer also saturates AASS horizons, and triggers reduction therein. This, in turn, may diminish acid loading from AASS horizons by immobilizing Al via a reduction-induced pH rise. However, soil pH rises slowly because the secondary minerals formed due to the oxidation of Fe sulphides will be gradually solubilized and produce acidity. This reaction pattern also explains the previous findings that controlled drainage or sub-irrigation (Österholm *et al.* 2015) and other measures such as liming (*e.g.* Åström *et al.* 2007) elevate soil pH very slowly.

The present study revealed that the reduction of Fe oxides hardly leads to the formation of Fe sulphides in boreal AS soils. Therefore, there is a risk of increased leaching of dissolved Fe²⁺ to watercourses, where it causes acidity and oxygen depletion upon oxidation and hydrolysis of Fe³⁺. In the fields, waterlogging up to the rooting depth might lead to similar consequences to those observed in the lysimeters, but at different

rates depending on the amount of available OC and soil temperature. It is possible that the drainage waters remain acidic even though they can be poorer in Al than before waterlogging. However, waterlogging only extended to layers below the rooting depth, *i.e.* the transition and PASS horizons low in DOC, which supposedly decreases the acid loading without any marked increase in Fe^{2+} in discharge waters.

Oxidation of Fe sulphides is assumed to occur when the lowering of groundwater allows the penetration of O_2 into PASS horizons. However, the present study suggested that the oxidation of Fe sulphides is also possible in anaerobic conditions, where NO_3^- acts as an electron acceptor. This reaction pattern may even start the acid generating reaction loop in slightly acidic transition layers, but also in circumneutral PASS horizons. The extraordinarily high proportion of reactive FeS in the soils on the coast of the Gulf of Bothnia suggests that prevention of the oxidation of PASS horizons is especially indispensable in these areas to avoid environmental hazards. Therefore, in these horizons, the maintenance of waterlogging and impermeability prevents anaerobic oxidation processes by restricting the diffusion/convection of NO_3^- .

The results of the present study revealed that in terms of environmental consequences, not only the chemical oxidation processes but also the transport processes that are dependent on the soil structure formed during soil ripening are important. The boreal coastal ASS soils are commonly fine grained and mostly contain clay and silt fractions (Åström and Björklund, 1997), but even coarse-grained AS soils exist (Boman *et al.* 2014). The clay soil of the PASS horizon monitored in the present study had a low hydraulic conductivity (IV). In coarser ASS soils, ripening and thus the emergence of detrimental environmental effects can be expected to occur more rapidly. Because knowledge of the impact of soil texture on ripening and subsequent environmental hazards is lacking, further studies are acutely needed. The impacts of different management systems on the on-site and off-site hazards of boreal AS soils compiled on the basis of the results obtained in this study are summarized in Table 7.

Table 7. *Desired (+), highly desired (++), harmful (-), extremely harmful (--) and not considerable (±) short-term impacts of different water management systems for boreal AS soils on aquatic and terrestrial ecosystems assumed to occur based on the results of this study.*

	Water management		
	Efficient drainage	Waterlogging	
		Up to topsoil	PASS of horizons
<hr/> Effect on aqueous ecosystem <hr/>			
Al loading	- -	++	+
Fe loading	-	--	±
Acidity	--	--	+
pH	--	+	±
<hr/> Effect on soil ecosystem <hr/>			
pH	-	+	+

Impact of water management on GHG emissions from boreal cultivated AS soils

On AS fields, the high N and OC pools in the Cg horizon give rise to concern for their potential to produce GHG emissions (I). Indeed, according to results obtained in Australia, N₂O emissions from AS fields were higher than those from non-AS soils (Macdonald *et al.* 2008, Denmead *et al.* 2010). Similar findings have also subsequently been reported in Denmark (Petersen *et al.* 2012) and in Finland (Uusi-Kämppe *et al.* 2012). In Australia, a laboratory experiment demonstrated N₂O emissions to be coupled with the oxidation of Fe sulphides (Macdonald *et al.* 2010), and this outcome was confirmed in later field experiments (Macdonald *et al.* 2011). The investigations on a boreal AS field suggest that the same reaction pattern reported in a warmer climate may also explain the high N₂O emissions in boreal conditions. The N₂O emissions appear to be attributable to acidic conditions, the abundance of OC and high soil moisture (Macdonald *et al.* 2011). These prerequisites are best met in the transition horizon.

In the course of present experiment, a separate gas emission study was conducted with the topsoil of all lysimeters (Simojoki *et al.*, 2012). In all lysimeters, the highest N₂O emissions were measured after NO₃⁻ fertilization at the beginning of the growing season. Later, the emissions from HWC and LWC were of the same order of magnitude and exceeded those from HWB (Simojoki *et al.* 2012). Their higher emissions can be explained by dissimilar reaction patterns. In HWC, where soil moisture fluctuated daily, the high N₂O emissions can be explained by denitrification. In LWC, in turn, high emissions can be taken to be attributable to the oxidation of Fe sulphides by NO₃⁻ in deep soil layers. In HWB, saturated permanently with water and having no NO₃⁻ formation, N₂O emissions were the lowest. Recent field observations in Finland indicated that N₂O emissions were lower when the water table was kept above the transition horizons by sub-irrigation (Uusi-Kämppe *et al.* 2012). This may be caused by a restricted drop in the water table to the transition and PASS horizons (Österholm *et al.* 2015). On the basis of these findings and those obtained in this study, it can be deduced that N₂O emissions from boreal AS fields are attributable not only to N fertilization and denitrification but also to the oxidation of Fe sulphides by NO₃⁻.

5. Concluding remarks

The continuous measurement of the soil redox potential along with other physical-chemical parameters developed in this thesis enable for the first time the monitoring of processes induced by different water management systems in boreal AS soils. The results obtained were consistent with the prevailing theory of redox potentials, but led to the rejection of some hypotheses that were developed from results gained in warmer conditions than those in boreal AS fields. The present results provide new conceptual background information on the processes induced by water management of AS soils and create a comprehensive basis to develop solutions for the mitigation of off-site hazards, especially in boreal AS soils.

The main outcomes of this thesis study were as follows:

1. The monolithic lysimeter concept developed in the present study enabled the creation of reduced conditions in soil and their maintenance throughout the 2.5-year experimental period. The study performed at three scales provided an opportunity to monitor redox processes and their consequences on-line in the controlled conditions of lysimeters and to validate the results in the parent field. The similarity between the lysimeter and field scales proved the concept developed in this thesis study to be a feasible method to investigate water management practices in boreal AS soils.
2. The response of soil to waterlogging appeared faster in the monoliths than in the field, giving valuable information on possible development patterns caused by the water management of AS fields. The large differences between pore and discharge water quality in the lysimeter study demonstrated water management to be a practicable option to control processes in the soil and affect the quality of leaching water. In fields, inertia related to the complex soil system evidently retards the response to water management, and the counteracting processes, such as the release of retained acidity from AASS horizons, mask the consequences in the short term. Therefore, further studies on the quality and quantity of retained acidity in boreal AS soils are needed.
3. Waterlogging of cultivated AS soil did not result in the notable formation of Fe sulphide. The probable reasons were 1) low soil pH favouring Fe-reducing microbes instead of SO_4^{2-} reducers, 2) a high amount of reactive, poorly ordered Fe hydroxides in the soil, 3) the low soil temperature slowing reaction rates, 4) the freshwater used in waterlogging not being able to assist the pH rise in reduction reactions and 5) low labile OC in horizons poor in root material. Nevertheless, a rise in pH due to the waterlogging lowered the toxic Al concentration in pore and discharge waters and prevented episodic high acidity peaks in discharge water.

4. Intensified drainage increased the proportion of PFP in the soil, and the influx and outflow of elements between the soil and the environment. It also increased the acidity of discharge water and its Al concentrations. The study revealed that ripening, commonly neglected, has to be taken into account in assessing the environmental consequences of AS fields.
5. The anaerobic oxidation of Fe sulphides appears to be possible in boreal AS soils where NO_3^- is leached from upper soil layers and in those having large N pools in the subsoil. The abundance of active microbes in PASS horizons, as well as the groundwater that occasionally drops to the PASS horizons, may contribute to GHG emissions. In addition, the oxidation of Fe sulphides by NO_3^- may also increase gas emissions, *e.g.* N_2O . These conclusions should be tested experimentally in further studies.
6. Some results obtained in this study contrasted with those obtained in warmer climates. The key explanatory factors were the low temperature and the use of freshwater in waterlogging instead of saline water. This study emphasised that new methods imported from dissimilar environmental and climatic conditions have to be assessed and tested locally, and national and/or regional knowledge of soils and their processes is therefore highly important.

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Appendix A *The summary of the determination of time series variables*

Paper	Variable	Abbreviation	Unit	Media	Measurement interval	Number of probes/samples/point	Scale, place	Method
II,III	Redox potential	E _h	mV	soil	every 10 min	50 probes	lysimeters/horizon	Pt-electrodes
	Temperature, pH, electrical conductivity	T _m , pH _m	°C, -		once a month	50 point		ISFET, conductivity meter
		pH _{pw} , EC _{pw} , pH _{dw} , EC _{dw}	- , dS m ⁻¹	porewater	every second week in summer, once a month in winter	50 samples		
			IV		- , dS m ⁻¹	discharge water	every week in summer, once a month in winter	10 samples
IV	pH, temperature, electrical conductivity	pH _{gw} , T _{gw} , EC _{gw}	- , °C, dS m ⁻¹	groundwater	once a month in summer, three times in winter	10 samples	field	
II	Volumetric moisture content	ε	m ³ m ⁻³	soil	every 10 min	30 probes	lysimeters/horizon	5TE probes
	Watertable on the lysimeters		m		4-10 times per week in summers, weekly in winters	10 tubes	lysimeters/pedon	tapemeter
IV	Groundwater level		m		once a month in summer, three times in winter	10 grounwater wells	field	
II,III	Temperature	T _m	°C			every 10 min	30 probes	lysimeters/horizon
II		T _a		air, in open space	3 probes		outdoor	thermopair
				air, among the RCG canopy	4 probes		compartment of	
				air, inside lysimeters insulation	5 probes		greenhouse	
III,IV	Total dissolved element concentration:		mg dm ⁻³	porewater	every second week in summer, once a month in winter	50 samples	lysimeters/horizon	ICP-OES
IV	Al, Fe, S, B, Ba, Ca, Cd, Co, Cr, Cu, K, Mg, Mn, Na, Ni, P, Pb, Si, Ti, V, Zn and Zr		mg dm ⁻³	discharge water	every week in summer, once a month in winter	10 samples	lysimeters7pedon	
			mg dm ⁻³	groundwater	once a month in summer, three times in winter	10 samples	field	
III	Dissolved organic matter	DOC	mg dm ⁻³	porewater	once a month in summer, three times in winter	50 samples	lysimeters/horizon	TOC-V
Summary	Dissolved nitrogen	TN	mg dm ⁻³					CPH/CPN
	NO ₃ ⁻	NO ₃ ⁻	mg dm ⁻³					Lachat
	NH ₄ ⁺	NH ₄ ⁺	mg dm ⁻³					